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STUDIES OF METHYL TIN CARBOXYLATES

by

P. B. SIMONS



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled,

STUDIES OF METHYLITIN CARBOXYLATES

submitted by Paul Bernard SIMONS, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Deo Gratias.

ABSTRACT

Four series of methyltin carboxylates have been prepared and studied. Infrared and nuclear magnetic resonance (NMR) spectroscopy and molecular weight determinations were used to study the structure of these compounds in solution and in the solid state.

Six trimethyltin carboxylates were studied in the first series. The previously known insoluble trimethyltin formate and trimethyltin acetate have been converted to a new, soluble form. The three trimethyltin chloroacetates have been found to be soluble, as prepared, in spectroscopic solvents, in contrast to their reported insolubility. Trimethyltin pivalate has been found to be readily soluble as prepared. Experimental results imply an equilibrium in solution between monomeric and associated forms for most trimethyltin carboxylates. It is suggested that the associated forms may be a cyclic structure, in contrast to the linear polymeric structure usually attributed to the insoluble form. Infrared spectra of trimethyltin mono- and dichloroacetate suggest that conformational isomers of these molecules are present.

The compounds studied in the second series consisted of five simple aliphatic dimethyltin dicarboxylates (formate, acetate, propionate, isobutyrate and pivalate), and five dimethyltin bis(halocarboxylates) (monochloro-, dichloro-, and tri-chloroacetate, monobromoacetate, and 2-chloro-2-methyl propionate). It is suggested that these compounds are capable of undergoing a condensation reaction to form tetramethyl-1,3-dicarboxylatedistannoxanes. Previously, hydrolysis of dimethyltin dicarboxylates was suggested as being the principle mode of formation. Infrared and NMR data have been inter-

preted as suggesting the C-Sn-C bond angle.

Dimethylchlorotin carboxylates were studied in the third series. Literature methods of preparing dimethylchlorotin carboxylates were found to produce an unusual material suggested as being a mixed trinuclear methyltin carboxylate composed of one molecule of dimethyltin dicarboxylate and two molecules of dimethylchlorotin carboxylate. Infrared and NMR data are believed to indicate essentially tetrahedral geometry about tin for these compounds.

Infrared, NMR and molecular weight studies of the three methyltin carboxylate stannoxanes (pivalate, trichloroacetate, and trifluoroacetate), which comprised the fourth series, are interpreted as suggesting a tendency toward dimerization in solution. A structure is proposed for some of these materials.

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CHAPTER I

INTRODUCTION

The beginning of synthetic organic chemistry is generally believed to stem from Woehler's synthesis of urea from ammonium cyanate, reported in 1828. The first compound containing an organic group bonded directly to tin was reported by Lowig only 14 years later.

Following Lowig's initial discovery many workers began research into the area that is presently known as organotin chemistry. The fund of knowledge concerning such compounds increased slowly but steadily over the years.

As a result of important applications of organic derivatives of silicon and lead, i.e. silicones and tetraethyl lead, a renewed interest in organotin chemistry did not occur until the late 1940's. Successful industrial application of organotin compounds has brought about vigorous research activity in industrial as well as academic laboratories. The greater portion of this work has centered on preparative aspects and potential industrial applications, such as catalysis, plastic stabilization, bacteriostatic activity, etc. Evidence of this can be found in an excellent review published in 1960 (1). Structural aspects of organotin chemistry are receiving nearly as much emphasis as preparative methods.

It is reasonable to assume that if the properties of the organic derivatives of the other members of group IV A (carbon, silicon, germanium, lead) were known that the properties of organic derivatives of tin should be quite similar. However, in comparing, for example, silicon and tin, in spite of a general similarity in physical properties,

one encounters very striking differences in chemical behavior. Silicon and tin have the same normal covalence and the same tetrahedrally directed bonding orbitals, which results in a similarity in physical properties of their organic derivatives.

The true nature of so-called organotin (II) compounds, i.e. a compound containing at least one tin-carbon bond with the tin atom being in the ground state electronic configuration, has been clarified by x-ray crystallographic studies. Olson and Rundle (2) found that diphenyltin, which was believed to be a tin (II) compound with the tin atom having the ground state electronic configuration like SnCl_2 , is actually a cyclic hexamer containing tin-tin bonds. The tin atom is therefore tin (IV) and not tin (II). The subject of organotin (II) compounds is discussed in a recent review by Neumann (3).

Several factors relevant to group IV A are listed in Table I. The differing chemical behavior of organotin and organosilicon compounds may be explained in the following way.

A. Effect of atomic radii: (Si, 1.17\AA ; Sn, 1.40\AA single covalent bond radius).

1. The larger size of the tin atom reduces the importance of steric factors. In addition the metal atom is less shielded by attached organic groups which facilitates attack by reagents.
2. Coordination numbers greater than four. In addition to the larger size of the metal atom, these elements may make use of d orbitals of the valence shell in bond formation, thus increasing their coordination state.

Although there is a similarity in this instance it is reasonable to state that silicon tends to use its d orbitals in double bonding

TABLE I

SOME FACTORS RELEVANT TO GROUP IVA

	C	Si	Ge	Sn	Pb
Pauling's Scale of Electronegativities (a)	2.5	1.8	1.8	1.8	—
Bond Dissociation Energy C-M, Kcal/mole [C ₃ H ₈] (b)	83-85	86 [Et-Si] (b)	56.7±2 [Et-Ge] (c)	46.2±2 [Et-Sn] (c)	30.8±2 [Et-Pb] (c)
Bond Length, Å (d) MCl ₄	1.755	2.00	2.06	2.30	—
Covalent radii, Å (e)	0.77	1.17	1.22	1.40	1.52
Dipole Moment (d) Debye units H ₃ MCl	1.87	1.28	2.03	—	—
Me ₃ MC ₆ H ₄ Cl (f)	—	1.70	—	2.16	—

- (a) L. Pauling, "THE NATURE OF THE CHEMICAL BOND", Cornell University Press, Ithaca, 3rd Edition, 1960.
- (b) W. C. Steele, L. D. Nichols and F. G. A. Stone, J. Am. Chem. Soc., 84, 4441, (1962).
- (c) H. A. Skinner in "Advances in Organometallic Chemistry", F. G. A. Stone and Robert West, Editors, Academic Press, New York, 1964, Volume 2, p. 98.
- (d) J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry", Tin Research Institute, 1955.
- (e) F. Albert Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1962.
- (f) H. H. Huang and K. M. Hui, J. Organometal. Chem., 6, 604, (1966).

arrangements in preference to increasing its coordination state while tin exhibits a strong tendency to increase its coordination state to five or six with a correspondingly reduced tendency to form double bonds (33).

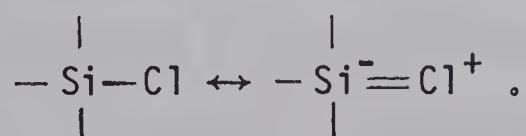
3. Increasing interatomic distances, usually associated with weaker bonding forces. Consequently bonds between carbon and tin are thermally less stable than carbon-silicon bonds.

4. Decreasing electronegativity causes the bonds of these elements with carbon and with elements more electronegative than carbon to be more polar than carbon-carbon bonds, thus rendering them more susceptible to attack by polar reagents. The alkyl tin halides behave as salts, halide ions being present in aqueous solution.

5. Interesting basic properties of R_3MOH type compounds. Trialkylsilanols are weak acids whereas trialkyltin hydroxides are definitely bases.

B. Charge distributions in organic derivatives of fourth group elements.

Organosilicon compounds have a lower dipole moment than carbon or organogermanium compounds. This is believed to be due to organosilicon compounds being able to expand their valence shell and participate in double bonds which makes possible a resonance system of the type



Although organotin compounds are also able to expand their valence shell, this type of resonance is drastically reduced in organotin compounds as indicated by the much higher dipole moment.

Hydrogen bonding studies (4) with ether and phenol using Ph_3MOH ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) compounds indicate that π bonding from oxygen to M is greatest for silicon, less for germanium and negligible for tin and lead.

Another aspect of the tendency toward double bond character is evidenced in comparing the bond length of silicon and tin tetrahalides. The Si-Cl bond is shortened 0.16\AA from the sum of the single bond covalent radii (observed: $2.00 \pm 0.02\text{\AA}$; calculated: 2.16\AA) while the Sn-Cl bond is only shortened 0.09\AA from the sum of the single bond covalent radii (observed: $2.30 \pm 0.03\text{\AA}$; calculated: 2.39\AA). That tin does have some tendency towards double bond character is evidenced by the nearly equal acid strength of substituted benzoic acids of the general formula $p\text{-R}_3\text{M-C}_6\text{H}_4\text{COOH}$, R being a methyl or ethyl group and M being silicon, germanium or tin (5). All of these acids are stronger than the corresponding carbon analogue. The greater acid strength is explained on the basis of the metal-phenyl bond having some double bond character, thus stabilizing the anion.

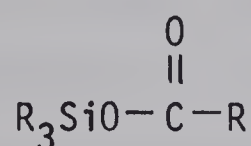
METHYLTIN CARBOXYLATES

Detailed structural arguments will be found in the body of this thesis under appropriate chapter headings. Assuming that the reader of this thesis is unfamiliar with the general topic of organotin carboxylates, a brief background of past structural theories is believed to be most desirable. The methyltin carboxylates may be classified into four separate groups each of which will now be described.

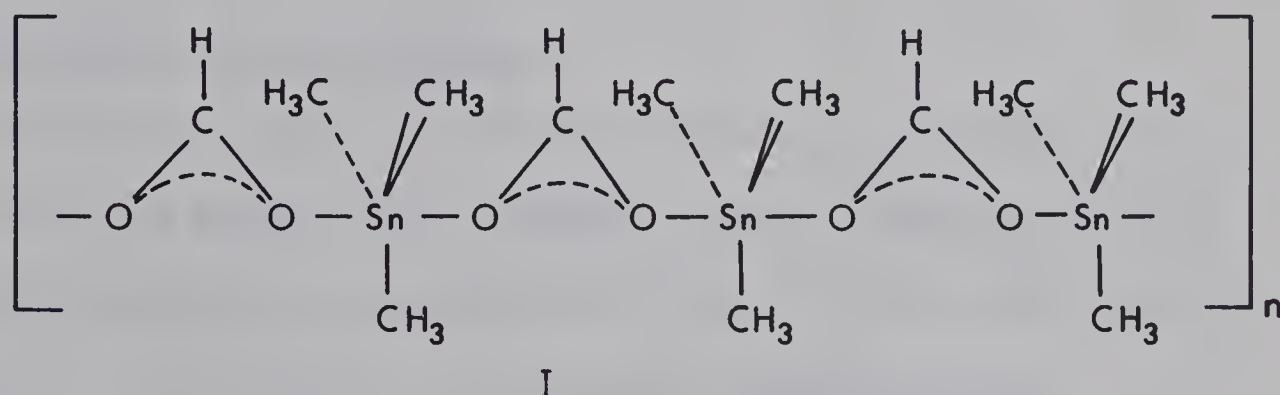
I. Trimethyltin carboxylates.

Trimethyltin carboxylates have been known for over 100 years.

However, the first study of their structure did not appear until the publication of Okawara, Webster and Rochow (6), who compared the infrared spectra of some methylacetoxysilanes and some methyltin carboxylates. The methylacetoxysilanes were studied in carbon tetrachloride solution and found to have normal ester-type linkages between the



silicon and the carboxylate moiety, while the methyltin carboxylates could only be studied in the solid state due to their rather remarkable insolubility. The insolubility was subsequently explained as being due to the tin compounds existing as salts composed of a planar trimethyltin cation and a carboxylate anion. This explanation was arrived at after a comparison of the infrared spectra of corresponding organotin and sodium carboxylates (6).

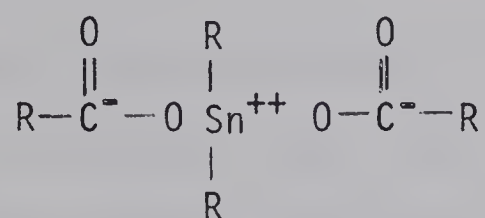


An alternative structural arrangement was proposed by Beattie and Gilson (7) who suggested that these compounds exist as infinite linear chain polymers consisting of planar trimethyltin groups with bridging carboxylate groups, five-coordinate tin being an essential feature of such structures. Such a structure would, of course, account for the insolubility of the compounds. Further investigation by Poller (8) and others has supported this bridging concept. However, lacking

an x-ray study, the subject cannot be regarded as unequivocally decided.

II. Dimethyltindicarboxylates.

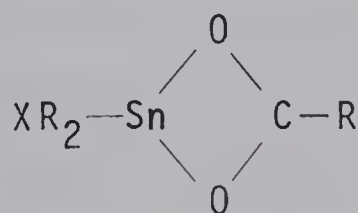
Dimethyltindicarboxylates were similarly suggested to exist as ionic materials composed of a linear dimethyltin cation and carboxylate anions. This explanation was in agreement with that suggested by Freeman (9), who concluded that dibutyltindiacetate was an ionic



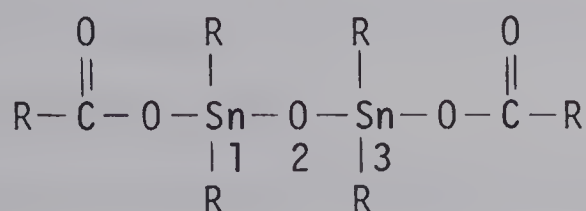
compound. The currently accepted structure of these compounds is analogous to that proposed for the trimethyltin carboxylates, i.e., linear dimethyltin groups bridged by carboxylate groups into infinite linear polymers.

III. Dimethylhalotin carboxylates.

Based on solid state and solution infrared spectra, and molecular weight studies in benzene (10), dimethyl halotin carboxylates have been assumed to exist as monomeric molecules with chelating carboxylate groups. The tin atom is of necessity five-coordinate.

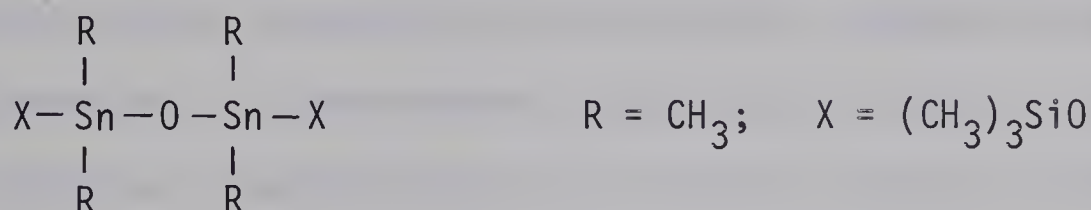


IV. Tetramethyl-1,3-dicarboxylate distannoxanes.



Organostannoxanes differ almost as greatly from organosiloxanes as the well known organosiloxanes (Silicones) differ from carbon ethers. The somewhat unusual physical and chemical properties of the siloxanes are believed to be due to the $d\pi-p\pi$ bonding of the silicon atom with the ether oxygen atom, whereas in organostannoxanes the observed physical and chemical behavior is believed to be due to the tendency of the tin atom to increase its coordination state from four to five.

The vast majority of structural studies of organostannoxanes have been concerned with compounds other than carboxylates; however, the conclusions have been assumed to apply also to carboxylate stannoxanes. The foundation upon which currently accepted structural concepts rely is the X-ray crystallographic study of tetramethyl-1,3-bis (trimethylsiloxy) distannoxanes (11, 12). This compound has



been found to exist as a dimeric species with dimerization resulting from a ladder-type structure with tin-oxygen coordinate bonds. Such a structure contains both four- and five-coordinate tin. Structural illustrations are presented in the body of this thesis. Again, unfortunately, no x-ray investigation of a carboxylate distannoxane has been reported. The validity of assuming that tetramethyl-distannoxanes have similar structures is thus subject to question.

Criterion for the Determination of the Configuration of the Trimethyltin and Dimethyltin Groups.

The vast majority of structural studies of organotin compounds

have utilized infrared spectroscopy. The portion of the spectrum from 600 to 500 cm^{-1} has proved very fruitful in that this region provides information regarding the configuration of the methyl groups bonded to tin. If the spectrum reveals two unambiguous absorptions (both the symmetric and asymmetric tin-carbon stretching vibrations) the configuration about the tin atom is non-planar or non-linear in the trimethyltin and dimethyltin moieties respectively. If only one absorption is observed this indicates a planar or linear configuration due to the symmetric stretching mode being infrared inactive. This simple criterion has been applied by many researchers with considerable success. The validity of this concept has been supported by x-ray analysis (13) in some cases.

Criterion for Determining the Coordination States of Tin.

Molecular weight determination of organotin compounds has proven to be the workhorse of experimental techniques available to organometallic chemists. The observation of molecular weights in marked excess of monomeric has been attributed to polymerization or dimerization with the tin atom increasing its coordination state by forming intermolecular coordinate bonds with some Lewis base-like portion of a neighboring molecule.

Nuclear Magnetic Resonance spectroscopy (NMR) has proven to be a powerful and versatile tool in coordination state studies. Sn^{119} NMR has been used to determine the magnetic environment about the tin atom. If all the tin atoms were in an identical environment then only a single resonance would occur. However, if the tin atoms were in more than one environment then more than one resonance should be observed in the absence of rapid exchange processes (14).

More recently Sn^{119} proton indirect spin-spin coupling has been used to deduce the coordination state of the tin atom (15, 16). The validity of this method has been demonstrated by spin-spin coupling studies of compounds which have been shown by x-ray crystallographic methods to possess either five-coordinate tin (17) or both four- and five-coordinate tin (12).

Bonding Concepts in Five- and Six-coordinate Tin.

It is well known that at least one of the groups bonded to tin must be of relatively high electronegativity if the coordination state of tin is to exceed four. The electronegative ligand-tin bond is polar with the tin atom possessing a partial positive charge. This partial charge is relieved by a donor ligand sharing a pair of electrons with the tin atom, necessitating an additional bond to tin.

Valence bond theory would indicate that the bonding in tin having a coordination state greater than four would necessitate using hybridized orbitals formed from 5s, 5p and 5d orbitals of tin. Thus five-coordinate tin would require dsp^3 hybridization (d_z^2sp^3 = trigonal-bipyramidal, $\text{d}_{x^2-y^2}\text{sp}^3$ = square pyramidal) and six-coordinate tin d^2sp^3 hybridization.

Some workers have discounted this explanation on the grounds that there may be appreciable disparity in the p and d energies and also that the 5d orbitals may be rather diffuse unless a number of highly electronegative substituents are present (18). Three-center molecular orbitals based on p atomic orbitals have been proposed as an alternative (19, 20). Bipyramidal structures, such as trimethyltin carboxylates, may be described as having sp^2 hybrid orbitals bonding methyl groups to tin, with the remaining p orbital participating in a

linear three-center bond with the two adjacent carboxylate oxygen atoms as illustrated in II.



II

Octahedral structures such as that assumed for dimethyltin-dicarboxylates may be thought of as having p orbitals participating in three-center bonds in the plane perpendicular to the dimethyltin portion of the molecule as illustrated in III.



III

If the tin-oxygen bonds are not equivalent, in that one type is appreciably more covalent than another, then the 5s character of the tin orbitals should become more uniformly divided instead of being concentrated in the bonds to carbon. McGrady and Tobias (20) have cited examples of this in their studies of several presumably trans octahedral dimethyltin compounds.

Valence shell electron pair repulsion theory (21) predicts that the lowest energy configuration of five valence electron pairs is a trigonal bipyramid and it has been suggested (13) that the more electronegative atoms are axial in such structures. Application of this theory to the methyltin carboxylates would predict that the dimethyl-halo-tincarboxylates and tetramethyl-1,3-dicarboxylatedistannoxanes would have non-linear methyltin groups.

Origin of the Problem.

The research upon which this work is based evolved from a preliminary study of carbon monoxide insertion reactions of the tin-transition metal bond. The complexity of the reaction indicated that a study of a simpler metal-metal bonded system would be judicious.

A brief description of this work, which is not immediately pertinent to the topic at hand, may be found in the appendix. It is sufficient for present purposes to state simply that a new soluble form of trimethyltin formate, previously known as an insoluble compound, was produced. In view of this rather surprising finding it was decided to expand the investigation to other types of organotin carboxylates. The organic moiety was limited to methyl to facilitate the use of NMR in obtaining structural information. It was anticipated that the removal of the restriction of insolubility would lead to an increased understanding of the nature of the rather complex interactions which evidently operate in alkyltin carboxylate compounds.

EQUIPMENT AND MICROANALYSES

Equipment.

1. The high vacuum system and sublimers.

A Pyrex high vacuum apparatus of conventional design was used in this investigation. Its major components were as follows:

- a. High vacuum pumping train consisting of a two stage mercury diffusion pump and a Cenco mechanical pump.
- b. McLeod pressure gauge.
- c. Low vacuum pump for the mercury side of the McLeod gauge.
- d. Delmar "O" ring and Pyrex ball and socket joint taps with stop cocks.
- e. Pyrex ball and socket and Delmar "O" ring cold traps.
- f. Various size "O" ring sublimers with stopcocks between sublimers and cold trap connection, and removable standard taper ground glass or "O" ring condensers.

2. Infrared spectrophotometers.

Infrared spectra to 400 cm^{-1} were obtained using Perkin Elmer 337 and 421 spectrophotometers. Spectra to 250 cm^{-1} were obtained using the model 421 spectrophotometer equipped with caesium bromide midrange interchange. Sodium chloride, potassium bromide and caesium bromide cells of several path lengths were used for solutions. Sodium chloride and potassium bromide plates and pressed potassium bromide discs were used for solid state spectra.

3. Nuclear Magnetic Resonance.

Proton NMR data were obtained using varian A-60, HR-100, HA-100

and A56/60A spectrometers. Where possible TMS was used as an internal standard, otherwise external TMS or an internal low field reference, i.e. CHCl_3 or C_6H_6 , was used. Accurate determination of the chemical shift and the spin-spin couplings was carried out using a Hewlett-Pacjard model 521C frequency counter and model 241A Hewlett-Packard oscillator. Most of the differential temperature NMR data were obtained using a Varian V4343 variable temperature probe and the HA-100 spectrometer; other variable temperature data were obtained with the A56/60A spectrometer, V4341/6057 variable temperature accesory and V5040 temperature controller.

4. Mass Spectrosocpy.

Mass spectra were determined with Metropolitan-Vickers MS-2 and AEI-MS-9 spectrometers.

5. Molecular Weight.

Molecular weights were determined in various solvents with a Mechrolab osmometer by the departmental microanalytical laboratory and by Schwartzkopf Microanalytical Laboratory, Woodside, New York.

6. Melting Point.

Kofler hot stage microscope and Gallenkamp melting point apparatus were used with both open and sealed capillary sample tubes. Melting points are uncorrected.

7. Gas chromatographic studies were conducted with the following:

Qualitative - Aerograph manual temperature programmer gas chromatograph model A-90-P.

Preparative - Nestor-Faust Prepomat.

Microanalyses.

Microanalyses were carried out by:

Alfred Bernhardt Mikroanalytisches Laboratorium
Mulheim, Germany.

Pascher Mikroanalytisches Laboratorium
Bonn, Germany.

Schwartzkopf Microanalytical Laboratory
Woodside, New York.

Microanalytical Laboratory
Department of Chemistry
University of Alberta.

CHAPTER II

TRIMETHYLTIN CARBOXYLATES

Prior to the experimental work upon which this thesis is based, the lower aliphatic carboxylic acid derivatives of trimethyltin hydroxide were reported to be insoluble in solvents commonly used in spectroscopic investigations. It is felt that for reasons of clarity and continuity of thought that the six trimethyltin carboxylate compounds prepared during the course of this investigation (trimethyltin formate, trimethyltin acetate, trimethyltin pivalate, trimethyltin monochloroacetate, trimethyltin dichloroacetate, trimethyltin trichloroacetate) are best discussed in detail as three separate but not necessarily independent types. The compounds will now be discussed in the following order: 1. Trimethyltin formate, 2. Trimethyltin acetate and trimethyltin pivalate, 3. Trimethyltin monochloro-, dichloro- and trichloro-acetate.

1. Trimethyltin formate.

Trimethyltin formate was prepared by Okawara, Webster and Rochow (6) by the reaction of trimethyltin hydroxide with formic acid. A striking property of the substance was its virtual insolubility in organic solvents, surprising in view of the appreciable solubility of compounds such as the trimethyltin halides and trimethyltin hydroxide. As was mentioned in the introduction, due to the solubility problem, these workers were restricted to the solid state for their infrared spectroscopic studies. The infrared absorptions they reported using pressed KBr discs and Nujol mulls as well as the absorptions reported (22, 23) for sodium formate in the solid state are given in Table II.

TABLE II

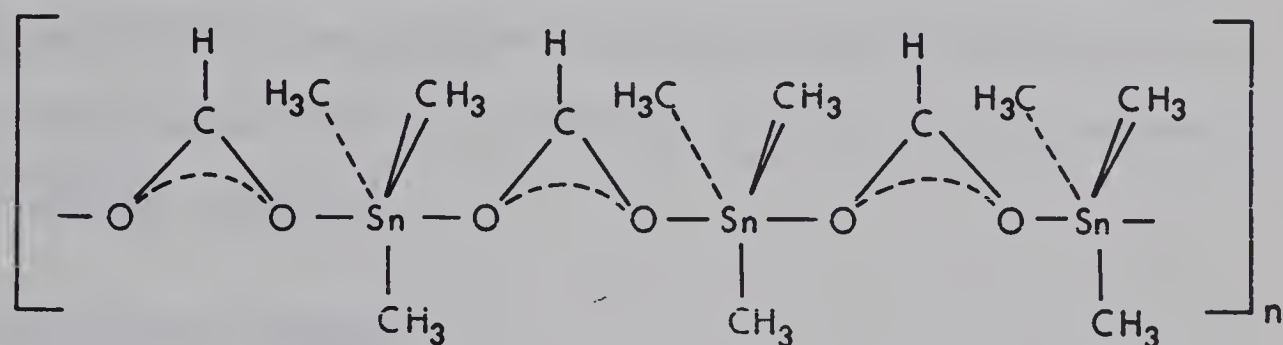
INFRARED SPECTRA FOR INSOLUBLE TRIMETHYLTINFORMATE AND SODIUM FORMATE*

$(\text{CH}_3)_3\text{SnOOCCH}_3$	NaOOCCH_3
1615 s	1620
1590 s	
1378 s	1377
1363 s	1365
1205 m	
1195 m	
	1070
790 sh	784
770 s	
552	

* Data of Okawara, Webster and Rochow (6) in Nujol and KBr.

Due to the reasonably close similarity in frequency of absorptions commonly assigned to carbonyl-carboxyl modes Okawara, Webster and Rochow (6) concluded that the compound was an ionic solid containing trimethyltin cations and formate anions. Furthermore, the presence of only one unambiguous absorption in the $600\text{-}500\text{ cm}^{-1}$ region was interpreted to indicate a planar arrangement for the methyl groups about the tin atom.

Shortly after the ionic structure hypothesis was put forth, Beattie and Gilson (7) suggested an alternative structural arrangement which was consistent with the observed infrared data. These workers suggested that the carboxylate group was functioning as a bidentate



I

ligand, bridging planar trimethyltin groups into infinite polymeric chains with the tin atom being five-coordinate.

The bridging carboxylate concept was favored by Janssen, Luitjen and van der Kerk (24) as a result of their study of a series of tri-alkyltin acylates in the solid state, in carbon tetrachloride solution, and as melts using infrared spectroscopy.

A particularly significant observation these workers reported was the fact that in the solid state the position of the carboxylate bands proved to be independent of either the size of the alkyl groups on tin or the length of the carbon chain of the carboxylic acid used.

Studies of the carbonyl stretching region of trimethyltin laurate at varying concentrations in carbon tetrachloride provided support for the bidentate bridging concept. Dilute solutions exhibited a single carbonyl absorption, with a second lower frequency band (essentially identical with that observed in the solid state) appearing at higher concentrations and increasing in intensity, at the expense of the higher frequency band, with increasing concentration. The entirely reasonable assumption that if the crystal has an ionic rather than polymeric lattice no association would appear in the dissolved state at any concentration, led to the abandonment of the ionic structure. Additional infrared (24, 25, 26, 27) and molecular weight (27, 28) studies were believed to indicate that, in general, trialkyltin acylates exist as infinite chain polymers in the solid and molten state and in concentrated solutions in non-polar solvents, but as monomeric species in dilute solutions.

Soluble Trimethyltin Formate.

Initially, conversion was carried out in an autoclave at high pressures of carbon monoxide, starting with the insoluble forms under cyclohexane. Subsequently, it was discovered that the conversion could be effected in essentially quantitative yield by heating the insoluble formate with cyclohexane in a sealed glass ampoule at 90-100°C for 12-24 hours. The solid is completely in solution when the tube is removed from the oven, and large, well formed fine needle clusters form on cooling. The material is readily soluble in chloroform and may be sublimed in high vacuum.

RESULTS AND DISCUSSION

The previously known insoluble trimethyltin formate has been converted in high yield to a new, soluble form. The solubility of the new form in chloroform at room temperature is of the order of 200 mg/ml. It is a remarkable fact that both forms are sublimable in high vacuum without interconversion, although the soluble form is appreciably more volatile.

Molecular Weight.

In solvents such as carbon tetrachloride or dibromomethane, soluble trimethyltin formate appears to be associated as the molecular weight is intermediate between that of a trimer and a tetramer. Monomeric behavior is observed in the donor solvent ethanol.

Infrared Spectra.

Arguments as to the structure of trialkyltin carboxylates, in both the solid state and in solution, have been largely based on the 1700-1400 cm^{-1} and 600-500 cm^{-1} regions of the infrared spectrum.

As has been pointed out, the bridging role for the carboxylate moiety has been generally accepted. One would expect the bridges to be disrupted in solution, and it has been found (25) that triethyltin acetate, with bands at 1572 cm^{-1} and 1412 cm^{-1} as a solid, absorbs in carbon tetrachloride solution at 1655 cm^{-1} and 1302 cm^{-1} ; the latter bands were considered to arise from a "free" carboxylate molecule, with structure analogous to that of an organic ester. The heavy metal atom was presumed (25) to reduce the frequencies below the normal organic ester range (29).

Carbonyl-Carboxyl Region.

The concentration dependence of the carbonyl-carboxyl region of the spectrum of soluble trimethyltin formate in chloroform solution is shown in Figure 1. The spectrum is strongly concentration dependent and it is reasonable to suppose that different species (or aggregates) are present at low and high concentrations. At low concentrations (Figure 1a) there is a strong absorption at 1650 cm^{-1} which is assigned to the carbonyl stretching mode of an unassociated formate group. The weak shoulder near 1600 cm^{-1} shifts to lower frequency and increases in intensity at the expense of the 1650 cm^{-1} band as the concentration is increased; ultimately, the 1580 cm^{-1} band is dominant, with the 1650 cm^{-1} band appearing as a relatively weak absorption (Figure 1d). The 1580 cm^{-1} band is assigned to the asymmetric carbonyl stretching mode of an associated formate group. The sequence of spectra in Figure 1 strongly suggests an equilibrium between associated and unassociated forms. These results closely parallel those of van der Kerk et. al. (25) for trimethyltin laurate. These workers, in common with others (26, 27) have assumed that the associated form, predominant at higher concentrations, has a linear structure. It is suggested, however, that the associated form may have a cyclic structure (such as IV). Such cyclic associated forms are compatible with much of the earlier data, both in solution and in the solid state. As will be discussed more fully, it is tempting to attribute a cyclic form to soluble trimethyltin formate, while retaining the conventional view that insoluble trimethyltin formate possesses a linear structure.

The carbonyl-carboxyl region of soluble trimethyltin formate was

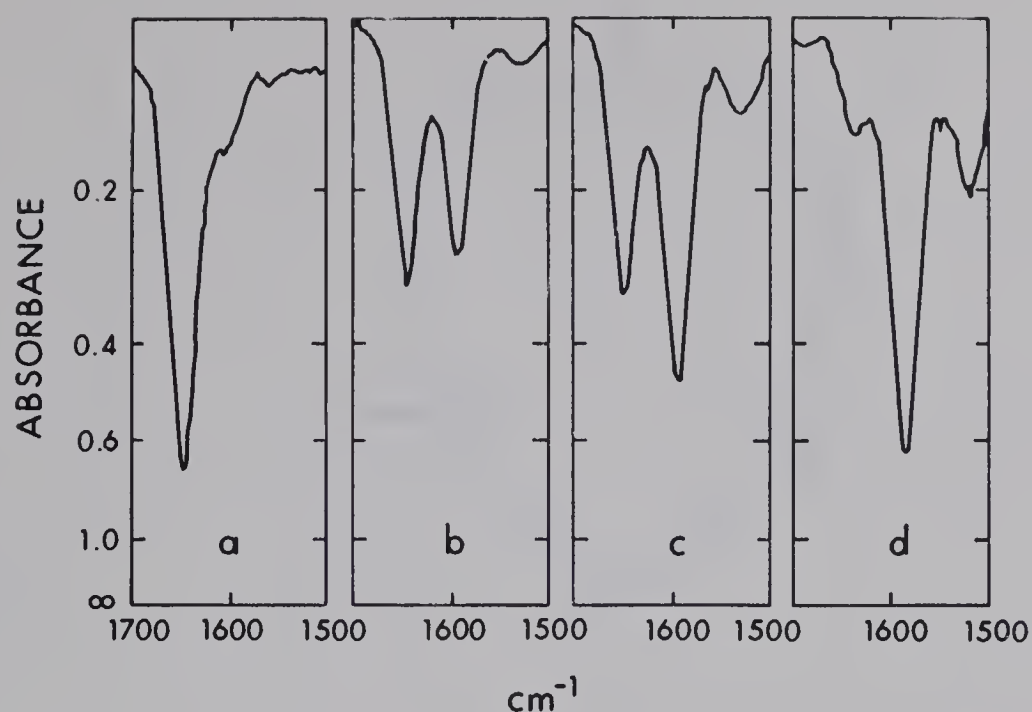


Figure 1. Effect of concentration on the infrared spectrum of trimethyltin formate in chloroform: a, 16.1 mg/ml, 0.5 mm cell; b, 26.5 mg/ml, 0.1 mm cell; c, 80.5 mg/ml, 0.1 mm cell; d, 161 mg/ml, 0.025 mm cell.

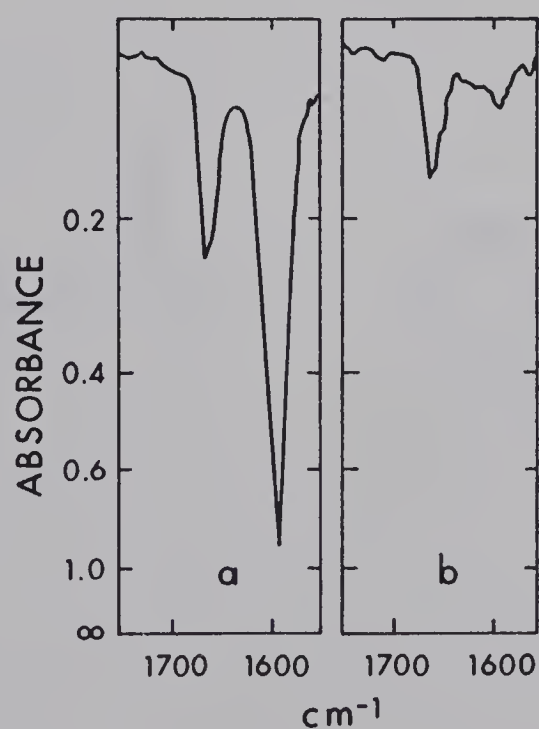
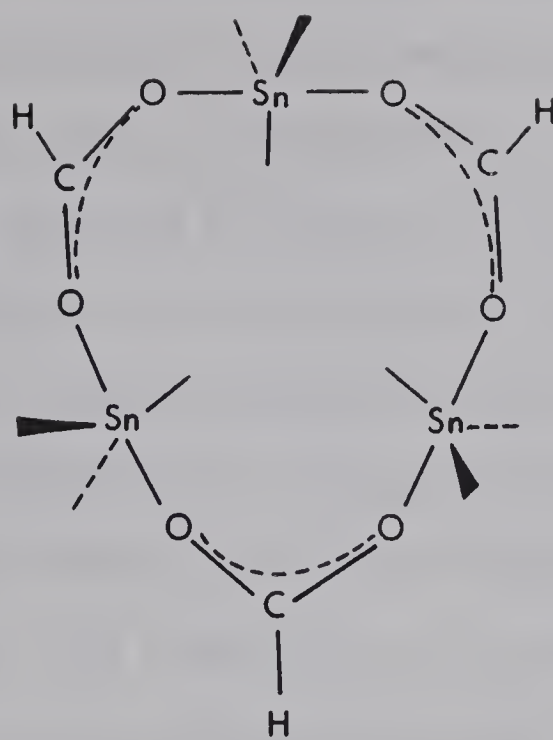
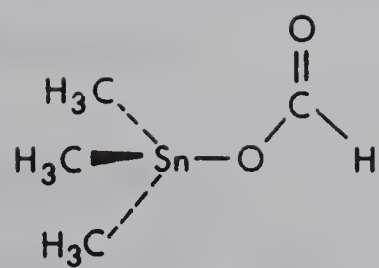


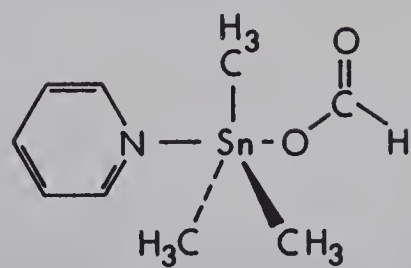
Figure 2. Effect of concentration on the infrared spectrum of trimethyltin formate in cyclohexane: a, warmed supersaturated solution; b, saturated solution at room temperature.



IV



V



VI

also examined in the non-polar solvent cyclohexane (Figure 2). Although the solubility in cyclohexane is much lower than that in chloroform, the same two bands appear, although shifted slightly to 1665 cm^{-1} and 1590 cm^{-1} . The spectrum of Figure 2a was obtained from a warmed, supersaturated solution, and the relatively high abundance of the unassociated (1665 cm^{-1}) species, compared to the chloroform solution (Figure 1d), may be explained as a temperature phenomenon. Variable temperature infrared studies of triocyltin acetate and tri-butyltin acetate (26) indicate that a temperature at or above the melting point of the solid or above room temperature for liquids, the free ester type linkage is favored. In the saturated though very dilute cyclohexane solution (Figure 2b) the relative absorbances of associated and unassociated formate can again be gauged from the intensities of the two bands; it is significant, however, that the proportion of the associated species is greater than in chloroform (Figure 1a). It is inferred that the unassociated form is favored in chloroform solution, either by the polarity of the medium or by some more specific interaction.

Tin-Carbon Stretching Region.

It is well established that an $\text{Sn}(\text{CH}_3)_3$ group involving a tetrahedral tin atom should give rise to two Sn-C stretching vibrations, while only one infrared active stretching band is expected for a planar $\text{Sn}(\text{CH}_3)_3$ group. Soluble trimethyltin formate [like the insoluble form (6)] in the solid state exhibits a single Sn-C stretching band at 555 cm^{-1} (Table III). In solution, however, (Figure 3a) a second band at 513 cm^{-1} clearly indicates the presence of nonplanar $\text{Sn}(\text{CH}_3)_3$

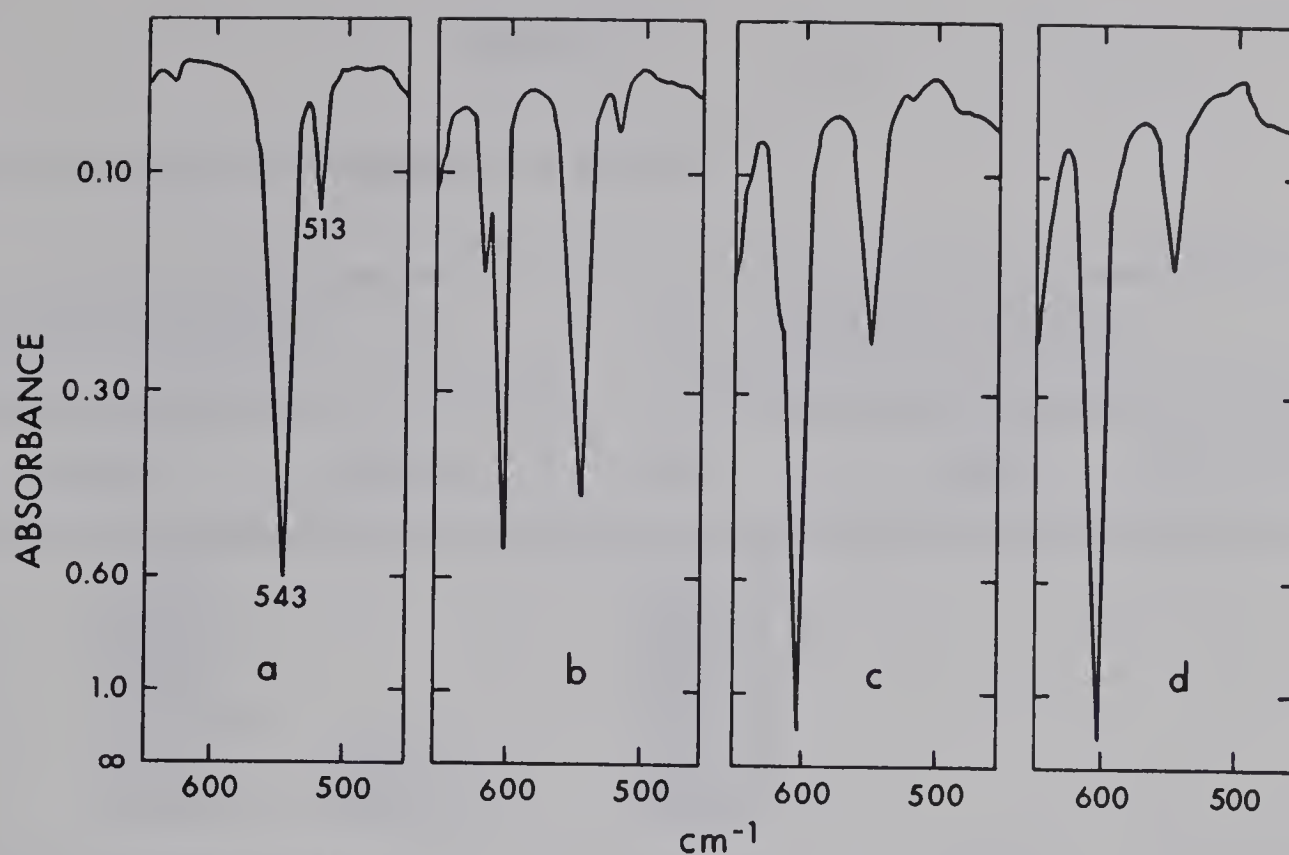


Figure 3. Effect of pyridine on SnC_3 stretching vibrations of trimethyltin formate in chloroform solution: a, no pyridine added, 0.083 M formate; b, 0.33 M pyridine, 0.069 M formate; c, 1.0 M pyridine, 0.042 M formate; d, 2.0 M pyridine, 0.028 M formate.

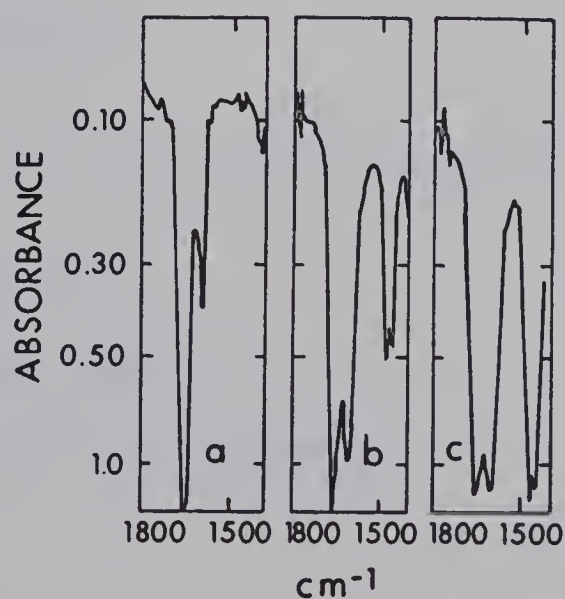


Figure 4. Effect of triethylamine on carbonyl vibrations of trimethyltin formate in chloroform solution: a, no triethylamine added, 0.065 M formate; b, 0.099 M triethylamine, 0.065 M formate; c, 0.34 M triethylamine, 0.065 M formate.

TABLE III

INFRARED SPECTRA FOR TRIMETHYLTIN FORMATES

(CH ₃) ₃ SnOCOH (soluble)				(CH ₃) ₃ SnOCOH (insoluble)			
CHCl ₃	(a)	KBr	Nujol	KBr	Nujol	KBr	(d)
		3000 w		3000 m			
		2930 m		2940 m			
		2860 m		2870 m			
		2790 vw		2800 vw			
		2710 w	2720 vw	2725 w			
		2370 w	2375 vw	2380 w			
1650 s							
1595 m	(b)	1592 s			1600 m	1615 s	
			1580 s, br	1580 s, br	1575 s	1590 s	
		1565 s					
1370 m-w		1368 s		1372 s		1378 s	
		1355 s	1355 s	1360 s	1360 m	1363 s	
		1198 w	1202 w	1205 w	1202 vw	1205 m	
		1190 m	1195 m	1195 m	1195 w	1195 m	
						790 sh	
		770 s	780 s	780 s, br	775 m	770 s	
550 m		562 s	555 s	555 s	550 s	552 s	
513 w							
430 mw		425 vw	425 vw				
			305 m				
(c)		(c)		(c)	(c)		

(a) CHCl₃ absorbs 800-600 cm⁻¹.

(b) Not present in dilute solution.

(c) Spectrum below 400 cm⁻¹ not available.

(d) From reference (6).

groups. It is assumed that the non-planar species in question, which is represented as V, gives rise also to the unassociated formate vibration at 1650 cm^{-1} .

Studies of Complex Formation.

Confirmation for the presence in solution of unassociated, tetrahedral trimethyltin formate molecules is provided by the spectra of Figure 3, in which the effect of adding pyridine to a chloroform solution is shown. It is well established that trialkyltin halides interact with bases such as pyridine (17) or dimethylsulfoxide (16, 30) to form five-coordinate complexes in which the tetrahedral arrangement of the free trialkyltin halide has been converted to a trigonal bipyramidal structure containing a planar SnC_3 unit. It is evident from Figure 3 that the intensity of the symmetric Sn-C stretching mode at 513 cm^{-1} decreases as the pyridine concentration increases; at high pyridine concentrations only the asymmetric 543 cm^{-1} vibration remains. This behavior parallels that observed (16) in the dimethylacetamide/trimethyltin chloride system, and it is reasonable to conclude that pyridine is converting the soluble formate (V) to the complex (VI).

It was of interest to observe the effect of complex formation on the carbonyl-carboxyl region of the spectrum. The base triethylamine was chosen for this purpose, because pyridine absorbs in the region of interest. The results are shown in Figure 4. The most significant result is the increase in intensity of a band at 1600 cm^{-1} . The band cannot in this case be attributed to an "associated" trimethyltin formate species in view of the findings concerning the configuration of the SnC_3 portion of the molecule. (It is considered unlikely that a trialkyltin derivative is capable of six coordination. No examples of

six-coordinate trialkyltin appear in the literature).

It is reasonable to suggest that the 1600 cm^{-1} band is due to a species like (VI), although the ionic character of the tin-formate bond and the geometry of the formate group may well differ from the conventional representation of the formula. Thus, the 1600 cm^{-1} frequency is intermediate between that of the unassociated species (V) (1650 cm^{-1}) and that of symmetrical or ionic formates such as (I) (1580 cm^{-1}).

NMR Spectra.

An initial conclusion of rather fundamental importance made possible by NMR is that the soluble formate is indeed a formate, and not, for example, the isomeric and as yet unknown trimethyltin-carboxylic acid. The NMR spectrum of the material (Figure 5) exhibited absorptions at 1.9τ and 9.4τ in an area ratio close to 1:9. The 9.4τ peak was clearly due to methyl groups on tin in view of the characteristic ^{119}Sn and ^{117}Sn satellites, as well as its location in a region where trimethyltin resonance commonly occurs. The low field proton signal could result from either a formate or carboxylic acid proton. The acid structure was ruled out by the lack of exchange of the low field proton with small amounts of added D_2O (Figure 6); the formate structure was confirmed by the observation of ^{13}C satellites of the 1.9τ peak with coupling $J(^{13}\text{C}-\text{H}) = 199\text{ cps}$ (saturated chloroform solution), a reasonable value for formates (31) (Figure 7).

As was mentioned in the introduction, a particular advantage of methyltin derivatives is the ease with which proton-tin spin-spin coupling constants can be determined. The coupling constants $J(^{119}\text{Sn}-\text{CH}_3)$ and $J(^{117}\text{Sn}-\text{CH}_3)$ provide invaluable information about



Figure 5.

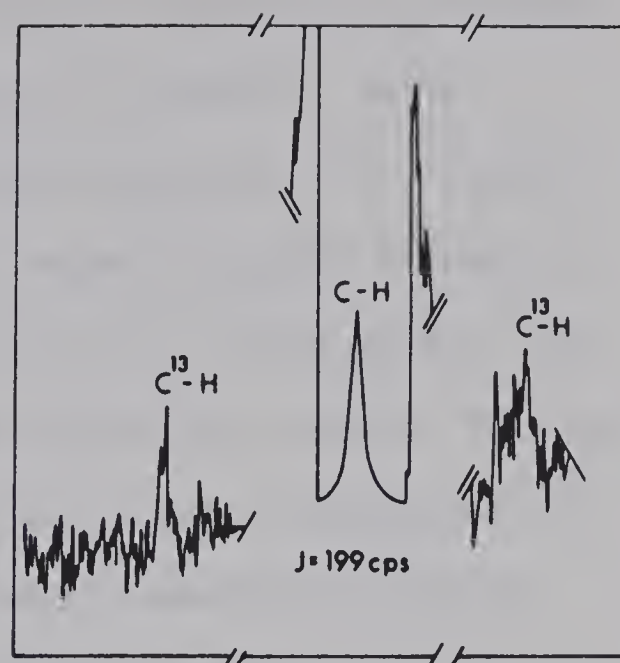


Figure 7.

Figure 5. NMR spectrum of trimethyltin formate in deuterochloroform.

Figure 7. Formate ^{13}C -H coupling.

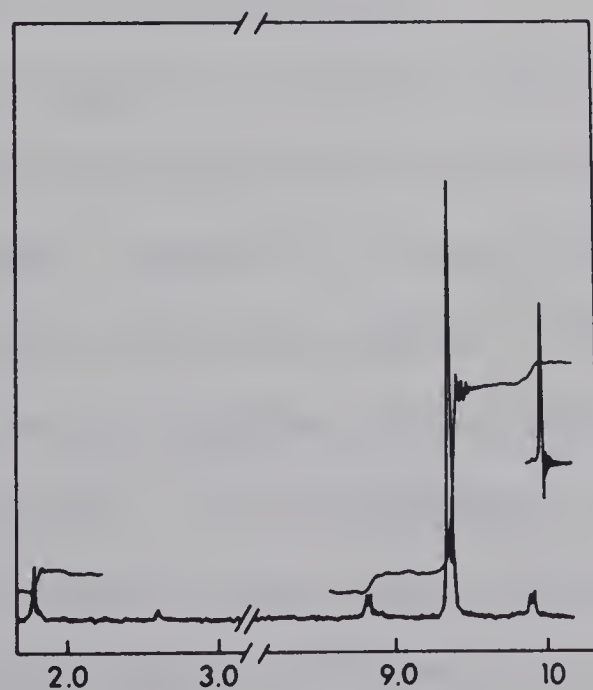


Figure 6. NMR spectrum of trimethyltin formate in deuteriochloroform, D_2O added.

the hybridization (32) and coordination number (15) of the tin atom.* Thus in tetramethyltin, J is 54.0 cps, while in trimethyltin chloride, J is 58.5 cps, reflecting a redistribution of s-character while retaining an approximately tetrahedral coordination for tin. In the pyridine adduct of trimethyltin chloride, known to contain five-coordinate tin with a planar trimethyltin group (17), J rises to 67.0 cps for a pyridine solution of trimethyltin chloride (15), and to 70.0 cps for a tetramethylene sulfoxide solution (16). Thus J can be used to distinguish between four- and five-coordinate trimethyltin species. Table IV lists the NMR results for trimethyltin formate.

Examination of the trends in coupling constants appears to be entirely consistent with the hypothesis set forth on the basis of the molecular weights and infrared results: that the soluble formate exists in solution as an associated and perhaps cyclic form containing five-coordinate tin, in equilibrium with an unassociated or monomeric form in which tin is four-coordinate.

The readers attention is directed initially to entries 1-4 of Table IV, in which the concentration is varied in CDCl_3 solution at constant temperature. Values of J range from 62.7 cps at the lowest concentration to 67.4 cps at the highest. This range falls between the approximate limits suggested in the previous discussion for four- and five-coordinate tin. It is reasonable to presume that what is actually being observed is the averaged coupling constants of four- and five-coordinate trimethyltin formate species in rapid equilibrium. This presumption is believed to be confirmed by the marked increase of

* Hereafter only the ^{119}Sn coupling constant will be used, denoted simply as J.

TABLE IV

PROTON MAGNETIC RESONANCE PARAMETERS FOR SOLUBLE TRIMETHYLTIN FORMATE

Solvent (ml)	Conc. mg/ml	Temp. (°C)	J(¹¹⁹ Sn-CH ₃) cps	J(¹¹⁷ Sn-CH ₃) cps
1. CDCl ₃ /CHCl ₃	48.0	33.5	62.7	59.9
2. CDCl ₃	52.6	33.5	63.9	60.4
3. CDCl ₃	68.2	33.5	66.7	63.8
4. CDCl ₃	150.0	33.5	67.4	64.4
5. CDCl ₃	48.0	40	62.0	59.2
6. CDCl ₃	48.0	50	60.5	57.7
7. CDCl ₃	48.0	-30	68.7	65.8
8. $\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{CHCl}_3 \\ \text{C}_5\text{D}_5\text{N} \end{array} \right\}$	0.75 0.25 36.0(a)	33.5	67.3	64.4
9. $\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{C}_6\text{H}_6 \\ \text{C}_5\text{D}_5\text{N} \end{array} \right\}$	0.5 0.1 0.4 80.0(b)	-40	68.5	65.5
10. $\left\{ \begin{array}{l} \text{DMSO-d}_6 \\ \text{CHCl}_3 \end{array} \right\}$	0.75 0.25 110.0(c)	33.5	69.9	67.0
11. DMSO-d ₆	200 (d)	33.5	70.4	67.6
12. Acetone-d ₆	210	33.5	66.4	63.5

(a) Molar ratio pyridine- d_5 /formate = 18:1.

(b) Molar ratio pyridine- d_5 /formate = 7:1.

(c) DMSO = dimethyl sulfoxide; Molar ratio DMSO-d_6 /formate = 20:1.

(d) Molar ratio DMSO/formate = 7.4:1.

TABLE IV CONT.

Solvent (ml)		Conc. mg/ml	Temp. (°C)	$\gamma(\text{CH}_3\text{-Sn})$ ppm	$\gamma(\text{H-COO})$ ppm
1.	$\text{CDCl}_3/\text{CHCl}_3$	48.0	33.5	9.44	1.89
2.	CDCl_3	52.6	33.5	9.42	1.90
3.	CDCl_3	68.2	33.5	9.44	1.92
4.	CDCl_3	150.0	33.5	9.45	1.91
5.	CDCl_3	48.0	40	9.44	1.89
6.	CDCl_3	48.0	50	9.43	1.87
7.	CDCl_3	48.0	-30	9.50	1.96
8.	$\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{CHCl}_3 \\ \text{C}_5\text{D}_5\text{N} \end{array} \right\}$	0.75 0.25 36.0(a)	33.5	9.70	
9.	$\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{C}_6\text{H}_6 \\ \text{C}_5\text{D}_5\text{N} \end{array} \right\}$	0.5 0.1 0.4 80.0(b)	-40	9.56	
10.	$\left\{ \begin{array}{l} \text{DMSO-d}_6 \\ \text{CHCl}_3 \end{array} \right\}$	0.75 0.25 110.0(c)	33.5	9.24	
11.	DMSO-d_6	200 (d)	33.5	(e)	(f)
12.	Acetone-d_6	210	33.5	9.96	2.37

(a) Molar ratio pyridine- d_5 /formate = 18:1.

(b) Molar ratio pyridine- d_5 /formate = 7:1.

(c) DMSO = dimethyl sulfoxide; Molar ratio DMSO-d_6 /formate = 20:1.

(d) Molar ratio DMSO/formate = 7.4:1.

(e) $J(^{13}\text{CH}_3) = 130$ cps.

(f) Peak broadened to about 100 cps.

coupling constants with concentration. The proportion of the associated, five-coordinate form relative to the four-coordinate monomer will increase at higher concentration; this is reflected in the higher average coupling constant.

The variation in coupling J as a function of temperature is given in entries 1 and 5-7 of Table IV. Values of J decrease from 68.7 cps at -30° to 60.5 cps at $+50^{\circ}\text{C}$. These are in agreement with a temperature dependent equilibrium, with the associated form favored by low temperature. Indeed, J at -30°C approaches the limiting value expected for five-coordinate tin, and the proportion of monomer present must be low.

Studies of Complex Formation.

The influence of pyridine- d_5 is shown in Table IV, entry 8. The dominant species, as in the case of the infrared studies, is the pyridine adduct IV. J has the value of 67.3 cps, which should be compared with the 65.2 cps for pyridine-trimethyltin chloride (15). It is believed that both values represent averages of complexed and free species, as a small equilibrium concentration of the latter would probably be present. As the temperature of the pyridine containing solution is lowered, (Entry 9, Table IV), J increases to 68.5 cps, in accord with the expected stabilization of the adduct (VI).

Solutions of soluble trimethyltin formate in the strongly coordinating solvent dimethylsulfoxide are measured in entries 10 and 11 of Table IV. In these cases, J is about 70 cps and there is evidently an insignificant amount of four-coordinate tin present.

2. Trimethyltin Acetate and Trimethyltin Pivalate.

These compounds have been grouped together as they may be viewed as structurally quite similar. Additionally, any observations which may be due to steric effects should be larger in the pivalate than the acetate.

Trimethyltin acetate has been known for over 100 years. A study of the literature indicates that it is insoluble in solvents commonly used in spectroscopic investigations (6, 25).

Trimethyltin pivalate has not been reported in the literature. It is isomeric with triethyltin acetate and not surprisingly is similarly readily soluble in typical organic spectroscopic solvents.

The structural arguments relating to trimethyltin formate discussed as the beginning of part 1 of this chapter are also applicable to these compounds and therefore will not be repeated.

Soluble Trimethyltin Acetate.

Trimethyltin acetate was prepared in its normal insoluble form according to the reaction



Conversion into soluble trimethyltin acetate was achieved in a manner identical to that described for trimethyltin formate. The process is virtually quantitative.

Soluble trimethyltin acetate is amply soluble for both infrared and NMR measurements; the solubility in chloroform is of the order of 50 mg/ml at room temperature. It should be noted, however, that the normal procedure for preparation of the acetate (33) involves recrystallization from light petroleum (boiling range 111-136°C); it

is certainly possible that during prolonged heating prior to crystallization, a partial conversion to the soluble form would occur.

RESULTS AND DISCUSSION

Molecular Weight Studies.

The molecular weight of trimethyltin acetate and trimethyltin pivalate in methylene bromide indicate a degree of association (D.A.) or polymerization between 1.0 and 1.3. Trimethyltin pivalate, but not trimethyltin acetate, was also studied in the non-polar solvent benzene and the polar, protic solvent ethanol.

As might be expected the molecular weights in ethanol are less than that of the monomer, indicating a possible decomposition of the compound, while those in benzene are essentially the same as those observed in methylene bromide.

The molecular weight data, although not conforming to a dimer, trimer or tetramer are considered as being consistent with a small amount of such entities being present, most likely in equilibrium with monomer.

Complete infrared data for trimethyltin acetate and trimethyltin pivalate are listed in Tables V and VI respectively. Figure 8 shows the infrared spectrum of a chloroform solution of trimethyltin acetate in the two regions of interest while similar information regarding trimethyltin pivalate in chloroform is illustrated in Figure 9.

Carbonyl-Carboxyl Region.

The relatively low intensity of the associated carboxylate bands indicates that the degree of association of the acetate is less than

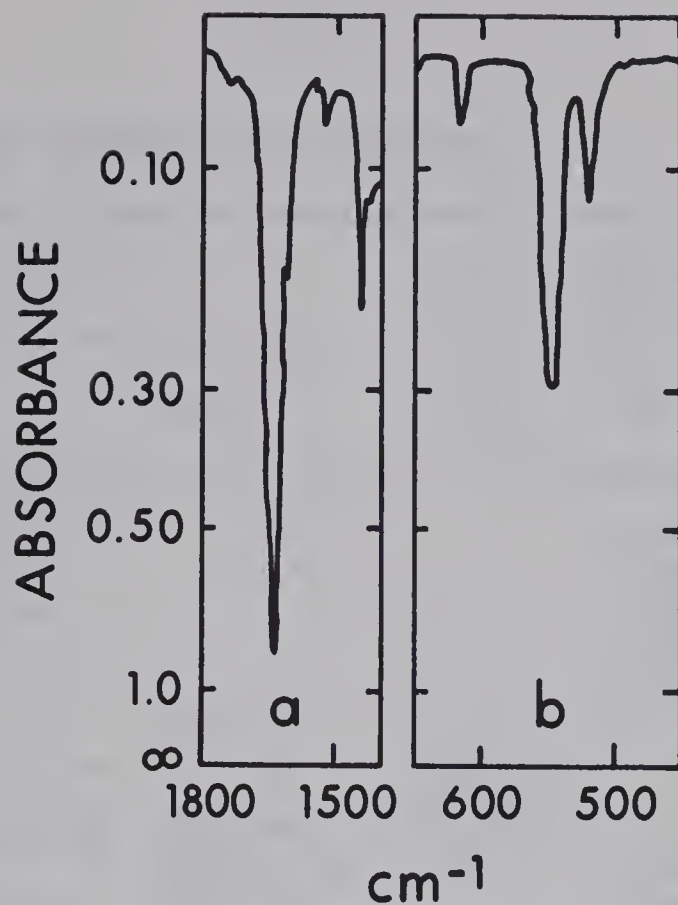


Figure 8. Infrared spectrum for trimethyltin acetate in chloroform solution: a, carbonyl stretching region; b, SnC_3 stretching region.

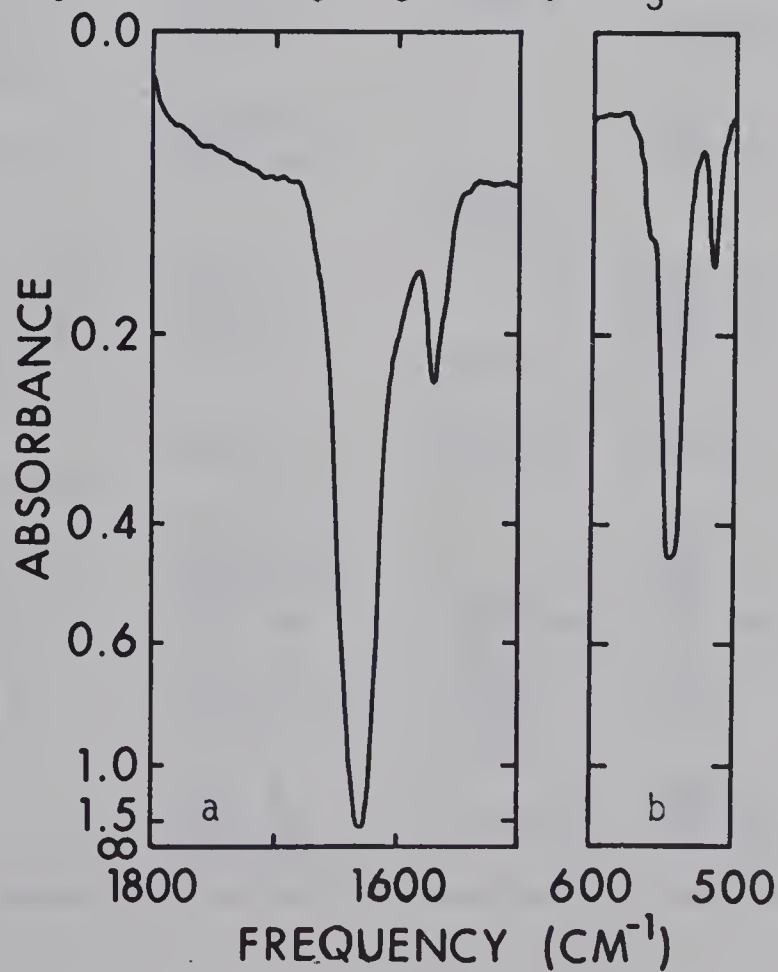


Figure 9. Infrared spectrum for trimethyltin pivalate in chloroform solution: a, carbonyl stretching region; b, SnC_3 stretching region.

TABLE V

INFRARED SPECTRA FOR TRIMETHYLTIN ACETATES.

(CH ₃) ₃ SnOCOCH ₃ (soluble)			(CH ₃) ₃ SnOCOCH ₃ (insoluble)		
CHCl ₃	KBr	Nujol	CHCl ₃	KBr	Nujol
	2990 w			3010 m	
	2910 w			2930 m	
	2815 vw			2830 w-m	
				2710 vw	
				2370 vw	
1678 s, sh		1677 w			
1658 vs			1650 vs		
1625 w-m	1600 m, sh	1608 ms	1615 m		
		1585 s, sh		1600 s, sh	1595 m, sh
	1570 vs	1570 vs		1575 vs, br	1565 s
1438 vvw, sh	1425 vs	1425 vs	1430 w-m	1425 vs	1420 s
1388 m		1383 ms	1380 s		1380 w-m
	1367 w	1370 m		1370 ms	1368 w-m
	1355 w				
		1360 m		1360 m	1355 w-m
	1345 w	1348 w-m		1348 m	1345 w
			1335 m		
1318 vs			1315 vs		
	1210 w-m	1206 w		1210 m	1205 w
	1197 w-m	1193 w		1195 m	1192 w
1050 vw	1052 vvw		1052 vw	1050 w	
	1020 w				
1015 w		1015 w	1018 m	1020 m	1015 w
	948 vw				
	785 s	775 m-s		780 s	773 s
	675 s	665 m-s		670 s	668 s
	618 w	608 vw	618 w-m	613 w-m	615 vw
			580 w		
544 m-s	558 s	548 m-s	553 s	553 s	553 s
515 w			523 m		
		490 w		495 m	495 w-m
425 vw		425 vw	425 vw	425 vw	425 vw

TABLE VI

INFRARED SPECTRA FOR TRIMETHYLTIN PIVALATE.

CHCl ₃	C ₆ H ₁₂	KBr	Nujol
	1713 vw		1681 w
	1659 sh		1668 w
1630 vs	1650 vs		
	1642 sh		
1570 w-m	1573 w	1601 vs	1595 vs
1478 m	1478 m	1566 s	1569 s
1455 w-m		1479 m-s	1478 m-s
1392 m	1392 m	1457 w	
1365 w, sh		1396 m-s	1397 m-s
1358 w-m	1358 w	1363 w, sh	
		1353 w, sh	
		1342 s	1345 s
1322 vs	1318 vs		
		1225 w, sh	1222 m, sh
	1200 vs	1214 m	1213 m
1175 w, br	1193 vs	1182 w	1182 w
1022 w, br	1010 w		1024 w
887 w	888 w	886 w	888 w
	800 w-m, sh	795 w	792 m
	782 m-s	785 m	782 m
	775 m	775 w-m, br	775 m, br
	755 m		
	718 w		
622 w-m	625 m, br	615 m	612 m
		558 m, sh	555 m, sh
545 m	550 m	552 m	550 m
	542 m		
512 w	518 w	520 vw	515 w
433 w	438 w, br	425 w, br	420 w, br

that of the pivalate or the formate. Although the lower degree of association of the acetate in relation to the formate may be explained on the basis of steric hindrance, the greater degree of association observed in the pivalate would indicate that additional factors are involved. Chelation of the pivalate group could well account for a portion of the associated carboxylate band intensity provided that the frequency of a chelated group is essentially identical to that of a bidentate, bridging carboxylate group.

Figures 8b and 9b show unambiguously the two tin-carbon stretching vibrations of the tetrahedral trimethyltin group.

At higher concentrations the "associated" 1580 cm^{-1} band of trimethyltin acetate reaches an intensity about equal to that of the "unassociated" 1650 cm^{-1} band. The spectral changes thus parallel those of soluble trimethyltin formate.

Concentration studies of trimethyltin pivalate in cyclohexane solution indicate that a small amount of association persists even at very low concentrations ($2.1 \times 10^{-1}\%$ w/v) and does not increase significantly even in saturated solution. This behavior is in marked contrast to that reported for trimethyltinlaurate (25) in carbon tetrachloride which exhibited no association at 2.3% w/v and the previously discussed trimethyltin acetate.

It is of interest that shoulders precede (1659 cm^{-1}) and follow (1642 cm^{-1}) the very strong unassociated carbonyl stretching mode of trimethyltin pivalate in cyclohexane. The origin of these shoulders is unknown. The broadening of carbonyl bands in chloroform, a phenomenon well established in the metal carbonyl field (34), presumably obscures the detail visible in cyclohexane, as no shoulders are observed in chloroform.

Trimethyltinacetate is not sufficiently soluble in cyclohexane to permit meaningful infrared spectroscopic study; however, shoulders precede (1678 cm^{-1}) and follow (1625 cm^{-1}) the very strong unassociated carbonyl stretching mode in a chloroform solution.

Solid state spectra of trimethyltinacetate exhibit shoulders preceding (1600 cm^{-1} , KBr; 1608 cm^{-1} , 1585 cm^{-1} , Nujol) the strong asymmetric carbonyl stretching mode (1570 cm^{-1} , KBr; 1570 cm^{-1} , Nujol). The corresponding symmetric absorptions are observed at 1425 cm^{-1} in KBr and 1425 cm^{-1} and 1383 cm^{-1} in Nujol.

The solid state spectrum of trimethyltinpivalate is somewhat different. Two strong asymmetric carbonyl stretching modes are observed in KBr (1601 cm^{-1} and 1566 cm^{-1}) and Nujol (1595 cm^{-1} and 1560 cm^{-1}) with the higher frequency absorption being more intense in both media. The corresponding symmetric absorptions are observed at 1396 cm^{-1} and 1342 cm^{-1} in KBr and at 1397 cm^{-1} and 1345 cm^{-1} in Nujol, with the lower frequency peak being more intense.

The 1585 cm^{-1} shoulder and 1570 cm^{-1} band of trimethyltin acetate and the 1566 cm^{-1} and 1560 cm^{-1} band of trimethyltinpivalate are believed to be due to the asymmetric carbonyl stretching mode of an associated acetate and pivalate group respectively. The assignment of the 1608 cm^{-1} , 1600 cm^{-1} band of the acetate and the 1601 cm^{-1} , 1595 cm^{-1} band of the pivalate is uncertain. These bands are $20\text{-}30\text{ cm}^{-1}$ higher than the value found for nearly all other associated trialkyltin carboxylates ($1560\text{-}1570\text{ cm}^{-1}$) and $30\text{-}60\text{ cm}^{-1}$ lower than that observed for unassociated carbonyl groups. As was mentioned in the first part of this chapter, van der Kerk, et. al. (25) have shown that the length of the alkyl groups on tin or on the carboxylate moiety does not greatly

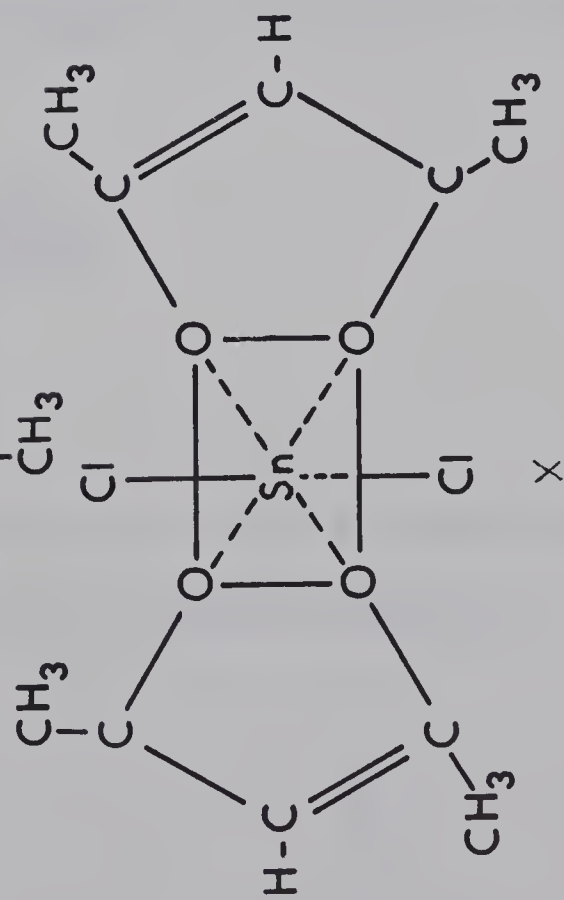
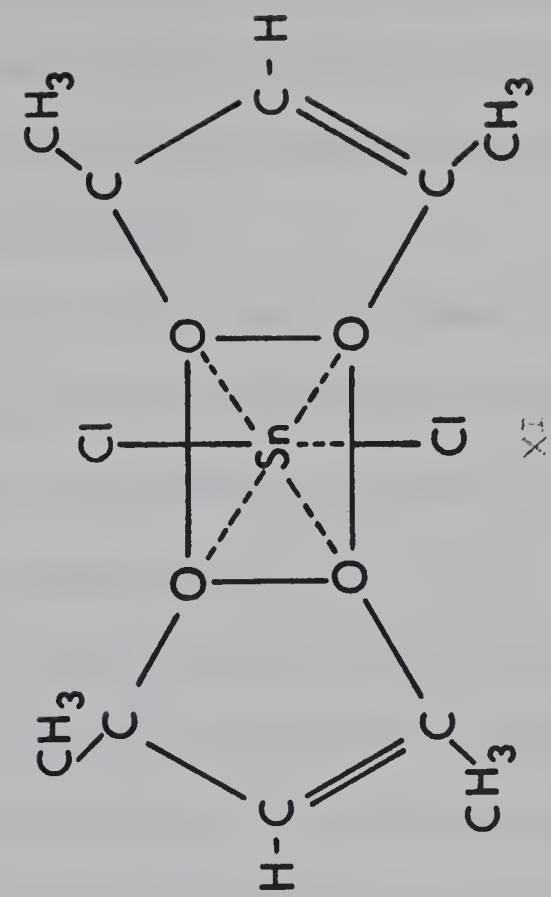
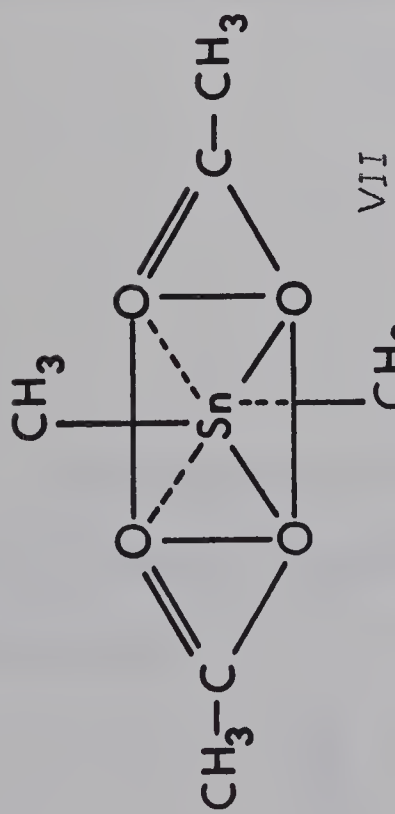
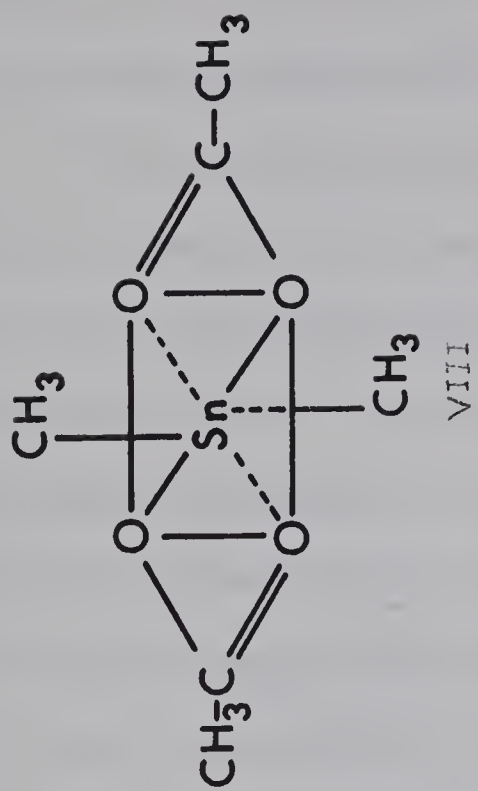
affect the frequency of the carbonyl stretching mode in the solid state. Thus the higher frequency observed in the acetate and pivalate must be due to some other effect.

Okawara, et. al. (35) have recently reported that dimethyltin-diacetate has a single asymmetric carbonyl absorption at 1607 cm^{-1} and symmetric absorption at 1380 cm^{-1} which remain essentially unchanged in the solid state, as a liquid film at 85°C or in carbon tetrachloride solution. These values are reasonably close to those observed in trimethyltin acetate and trimethyltin pivalate. It is not unreasonable to assume that the origin of the absorption is common to all three molecules. It has been suggested (35) that the absorption arises from a bidentate carboxyl group with an inequality in the tin-oxygen bonds.

An unsymmetrically coordinated carboxyl group, although lacking precedent, is an attractive explanation for the 1607 and 1380 cm^{-1} bands, and for bands in the same region in other compounds to be discussed later. It is important that this suggestion should not be confused with the representation shown in the canonical forms VII and VIII, which of course are intended to suggest the equivalence of the two C-O bonds; the resonance hybrid with equivalent Sn-O and C-O bonds is better represented as IX. The distinction between canonical forms and distinct structures in this case rests upon different positions of the nuclei. There has been some controversy (perhaps in part semantic) concerning postulated isomers of $\text{trans O}_2\text{Sn}(\text{acac})_2^*$ (36), which some took to be equivalent to the canonical forms X and XI (37).

It is of interest to consider the postulated unsymmetrical carboxylate coordination from the chemical bonding standpoint.

* acac = acetylacetonate.



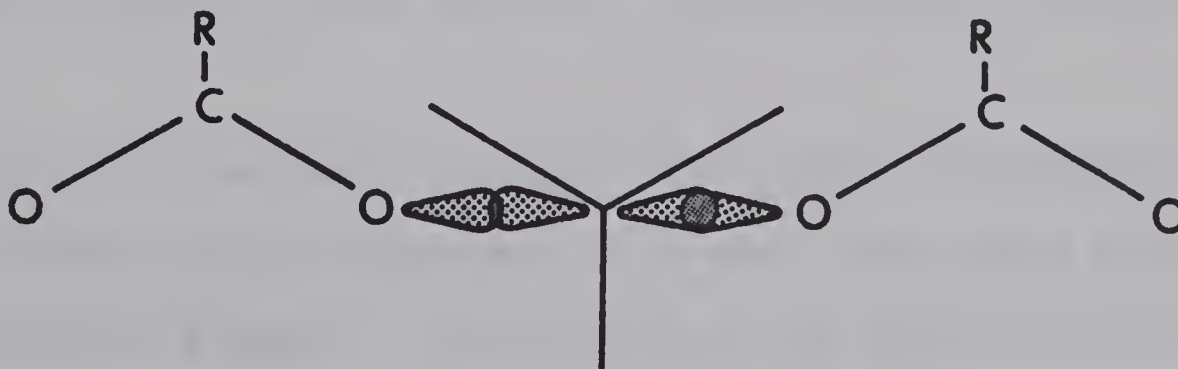
The two "normal" explanations used to explain the bonding in five-coordinate tin (1. rehybridization of the tin orbitals from sp^3 to dsp^3 , 2. three center $p\sigma$ molecular orbitals) involve assumptions which could invalidate them in the present case.

If the molecule is associated in the solid state, (either as a linear polymer or in some cyclic system) the tin atom would of necessity have five neighboring atoms. The most common structural arrangement used in such cases is that of a trigonal bipyramid. If this structural arrangement is used, five tin orbitals are required necessitating rehybridization involving 5s, 5p and 5d orbitals. Neglecting the orbital energy separation problem mentioned in the introduction, it is not clear why one presumably axial orbital should be preferred over another of presumably identical energy and configuration (XII).



XII

Three-center $p\sigma$ molecular orbitals would require unequal overlap of the tin p orbital by two different carboxylate oxygen p orbitals as in II.



II

The following alternative to the foregoing proposals departs somewhat from conventional structural concepts. The tin atom is considered to have five nearest neighbor atoms, however, only four of these atoms (three carbons and one oxygen) are bonded to tin by covalent type bonds. The remaining oxygen atom (formally the carbonyl oxygen of a different carboxylate group) is drawn toward the tin atom by presumably dipole-dipole interaction forces. The metal atom is thus formally five coordinate. The structure could perhaps be more correctly viewed as being a distorted tetrahedron with the methyl groups approaching a common plane and an additional atom present but not covalently bonded to the central metal atom. Figure 10 illustrates the postulated structure along with the monomeric and symmetrically bridged dimer structures. Two examples of this postulated structure have been established by recent X-ray crystallographic studies (39, 40, 41). The tin atom in (4-bromo-, 1, 2, 3, 4-tetraphenyl-1, 3,-butadienyl)dimethyltin bromide is five-coordinate. Nearly normal bond lengths were observed for ligands covalently bonded to tin (Sn-Br 2.507 Å), however, the bridging bromine atom-tin "bond" 3.769 Å is only 0.4 Å shorter than the sum of van der Waals radii 4.15 Å (39). Distorted tetrahedral geometry about tin is indicated by the 130.3° C₁-Sn-CH₃ bond angle. Five coordinate tin, distorted trigonalbipyramidal geometry and a long bridging chlorine-tin "bond" have been found in bipy-(OC)₃ClMoSnCH₃Cl₂ (41).

Although intramolecular halogen-tin or oxygen-tin coordination may be a rather general phenomenon, it is most likely not a determinative structural element. It may operate to the extent permitted by the primary structural features, with consequent wide variation in

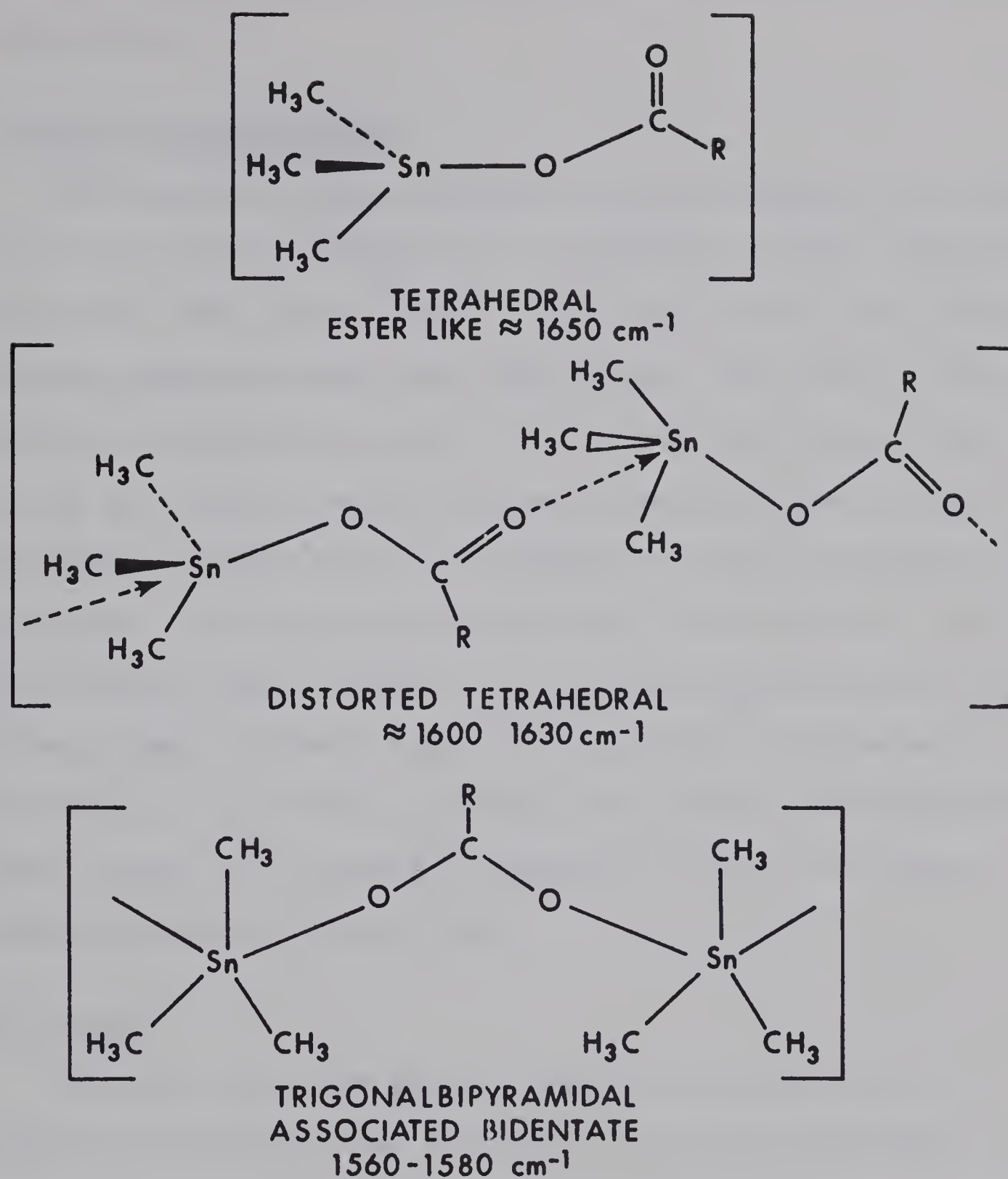


Figure 10. Postulated carboxyl bridging structures.

bond lengths, bond angles, and degree of covalent character within the bridging bonds (41).

Tin-Carbon Stretching Region.

The presence of bands assignable to both the asymmetric and symmetric tin carbon stretching modes in trimethyltin pivalate (552 cm^{-1} and 520 cm^{-1} , KBr; 550 cm^{-1} and 515 cm^{-1} , Nujol) in the solid state is in marked contrast to the single band (558 cm^{-1} , KBr; 548 cm^{-1} , Nujol) observed in trimethyltin acetate. This observation is surprising in view of the solution spectra and molecular weight data which seemed to indicate a greater degree of association in the pivalate than in the acetate. It is considered possible that this difference is due to the greater steric hindrance of the pivalate group decreasing the tendency toward presumably symmetrical association of the molecule. The presence of the bands is also consistent with the distorted tetrahedron concept just discussed in connection with the postulated unsymmetrical bridging pivalate group.

NMR Spectra.

The results of an NMR study of trimethyltin acetate and trimethyltin pivalate are given in Tables VII and VIII respectively. Trimethyltin acetate spectra (Figure 11) exhibits a single sharp resonance at 9.47τ with $\text{CH}_3\text{-Sn}$ Coupling J 58.5 cps and a single sharp resonance at 7.99τ in the ratio of 3:1. Trimethyltin pivalate spectra show a single sharp resonance at 9.54τ with $\text{CH}_3\text{-Sn}$ Coupling J 57.3 cps and a single sharp resonance at 8.85τ in the ratio 1:1. The lower field resonance in both cases is clearly due to the protons of the alkyl group of the respective carboxylic acid.

TABLE VII

PROTON MAGNETIC PARAMETERS FOR SOLUBLE TRIMETHYLTIN ACETATE (a)

Solvent	Temp. °C	$J(^{119}\text{Sn}-\text{CH}_3)$ cps	$J(^{117}\text{Sn}-\text{CH}_3)$ cps	$\gamma(\text{CH}_3-\text{Sn})$ ppm	$\gamma(\text{CH}_3-\text{COO})$ ppm
CDCl_3	33.5	58.5	56.0	9.47	7.99
CDCl_3	50.0	58.2	55.7	9.50	7.98
CDCl_3	-30	58.1 (b)		9.46	7.95
$\text{CDCl}_3/\text{C}_5\text{D}_5\text{N}$ (c)	33.5	65.8	63.1	9.54	8.18

(a) All measurements on solutions which were initially saturated at room temperature; estimated solubility is 50 mg/ml at room temperature.

(b) Signal broadened by precipitation of solid; ^{117}Sn - ^{119}Sn satellites not resolvable under these conditions.

(c) CDCl_3 0.75 ml; pyridine- d_6 0.25 ml; estimated molar ratio pyridine- d_6 /acetate = 10.5:1.

TABLE VIII

PROTON MAGNETIC PARAMETERS FOR TRIMETHYLTIN PIVALATE.

Solvent	Conc. mg/ml	Temp. °C	$\gamma(\text{CH}_3\text{-Sn})$	J^1 cps	J^2 cps	$\gamma[(\text{CH}_3)_3\text{COO}]$
CDC1 ₃ C ₆ H ₆	96.6	75	9.54	57.5	54.9	8.83
CDC1 ₃ C ₆ H ₆	96.6	50	9.54	57.5	55.0	8.85
CDC1 ₃ C ₆ H ₆	96.6	33.5	9.54	57.3	55.0	8.85
CDC1 ₃ C ₆ H ₆	96.6	0	9.53	57.5	54.8	8.86
CDC1 ₃ C ₆ H ₆	96.6	-20	9.54	57.8	55.3	8.88
CDC1 ₃	133.2	33.5	9.39	59.0	56.9	8.73
CDC1 ₃ } C ₆ H ₆ } C ₅ H ₅ N } .375 .625	36.2(a)	75	9.41	65.1	62.2	8.78
CDC1 ₃ } C ₆ H ₆ } C ₅ H ₅ N } .375 .625	36.2(a)	50	9.40	65.8	62.9	8.78
CDC1 ₃ } C ₆ H ₆ } C ₅ H ₅ N } .375 .625	36.2(a)	33.5	9.40	66.1	62.4	8.78
CDC1 ₃ } C ₆ H ₆ } C ₅ H ₅ N } .375 .625	36.2(a)	0	9.39	66.7	63.7	8.78
CDC1 ₃ } C ₆ H ₆ } C ₅ H ₅ N } .375 .625	36.2(a)	-20	9.38	67.0	64.0	8.77

(a) Molar ratio pyridine-d₅/pivalate = 56:1.

$J^1 = {}^{119}\text{Sn-CH}_3$; $J^2 = {}^{117}\text{Sn-CH}_3$.

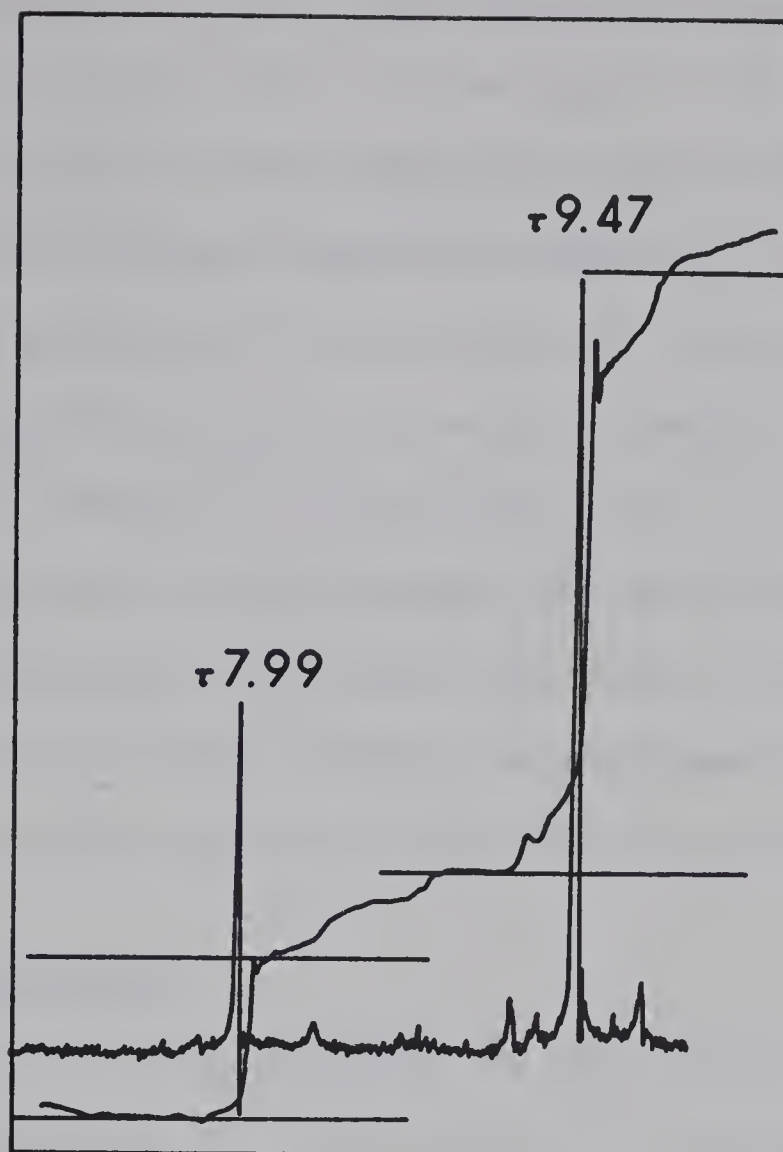


Figure 11. NMR spectrum for trimethyltin acetate in deuteriochloroform.

Examination of Tables VII and VIII reveals virtually no change in J with temperature for either compound. The change in J of trimethyltin pivalate as a function of concentration is very small (≈ 1.7 cps). The low degree of association as indicated by molecular weight and infrared studies is in good agreement with the small value of J .

It seems likely that the value of J for monomeric four-coordinate tin and the postulated unsymmetrically bridged associated five-coordinate tin are nearly identical, in marked contrast to the formate case. Presumably some type of associated species predominates at low temp-

eratures. If the value of J for this associated five-coordinate tin species were significantly different from that of four-coordinate tin then a definite change in J with temperature should be observed. Lack of change therefore indicates essentially identical J values.

It should be made clear that the value of J observed for trimethyltin acetate and trimethyltin pivalate is essentially the same as that observed for trimethyltin chloride (58.5 cps). If J is indicative of the hybridization of the tin orbitals this would appear to suggest a tetrahedral or distorted tetrahedral arrangement of groups bonded to tin with essentially sp^3 type orbitals, an arrangement consistent with the unorthodox bonding suggested in the infrared discussion.

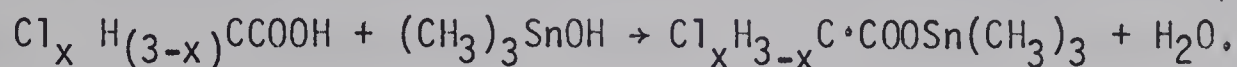
Complex Formation Studies.

Addition of pyridine- d_5 increases the magnitude of J to about 66 cps for both compounds at room temperature. A variable temperature study of trimethyltin pivalate-pyridine d_5 complex revealed little change in the magnitude of J (66.1 cps/ 33.5°C; 67.0 cps/ -20°C) approaching the limiting value of 70 cps. It is reasonable to assume that the pyridine complex is less stable than that with trimethyltin formate, a reasonable conclusion on steric grounds.

These studies support the postulate that the associated form of trimethyltin pivalate is of a special type. The magnitude of J for pure trimethyltin pivalate changes very little with either temperature or concentration, but as discussed above increases markedly on adding pyridine. This behavior should be contrasted with that of trimethyltin formate in which the magnitude of J is essentially identical for the pure compound at low temperature ($J = 68.9$ cps/ -30°C) and the pyridine complex at low temperature (68.5 cps/ -40°C).

3. Trimethyltin monochloroacetate, Trichlorotin dichloroacetate and trimethyltin trichloroacetate.

These three compounds were prepared by Okawara, Webster and Rochow (6) by the reaction of the appropriate chlorine substituted acetic acid with trimethyltin hydroxide.



The materials were reported to be insoluble, and consequently were studied in the solid state only. The structural arguments previously discussed concerning insoluble trimethyltin formate were also believed applicable in this case.

Results and Discussion.

The trimethyltin monochloroacetate, dichloroacetate, and trichloroacetate used in this study were prepared by the same reaction route used by the previous workers. All of the compounds are soluble in chloroform as prepared. In view of the lack of experimental details regarding Okawara et. al.'s preparation of these compounds, a comparison of preparative details is not possible. It should be pointed out however, that the initial aqueous reaction mixture of this study was evaporated to dryness on a steam bath. It is possible that the key factor in obtaining these soluble materials, as was the case with soluble trimethyltin formate and acetate, is the heating of the compounds in a suitable liquid for a suitable period of time. However, in the course of this work, insoluble forms of any of the chloroacetates have not been observed. The estimated solubilities of the compounds prepared in this study in chloroform at room temperature are as follows: monochloroacetate, 96 mg/ml; dichloroacetate, 83 mg/ml;

trichloroacetate, 70 mg/ml.

Molecular Weight Studies.

Values for the molecular weights of the three trimethyltin chloroacetates are given in Table IX. All three compounds show a small degree of association between 1.0 and 1.2 in dibromomethane with the values in carbon tetrachloride tending to be somewhat higher. The precision of the osmometric measurements was rather poor, and was not sufficient to detect the trend to increasing association that might be expected at higher concentrations.

Infrared Spectra.

As already noted, the chloroacetate esters have been found to be amply soluble for infrared investigation in both carbon tetrachloride and chloroform solution. The infrared spectrum of the dichloroacetate is discussed first since it raises a number of interesting questions.

The spectrum of trimethyltin dichloroacetate in carbon tetrachloride solution is strongly concentration dependent, and reveals much information regarding probable assignments and structures (Figure 12). As has been pointed out earlier in this chapter, such concentration dependence has been observed in trimethyltin formate and trimethyltin laurate (25); it is attributed to the equilibrium between unassociated and associated forms, in which both ester-like and bridging carboxylate groups are present. The most striking effect of increasing concentrations is the increase in intensity of the bands at 1652 cm^{-1} and 1368 cm^{-1} relative to the $1708\text{-}1687\text{ cm}^{-1}$ doublet and the 1330 cm^{-1} band. The bands which gain intensity at higher concentration are most probably due to an associated form; therefore, the 1652 cm^{-1} and

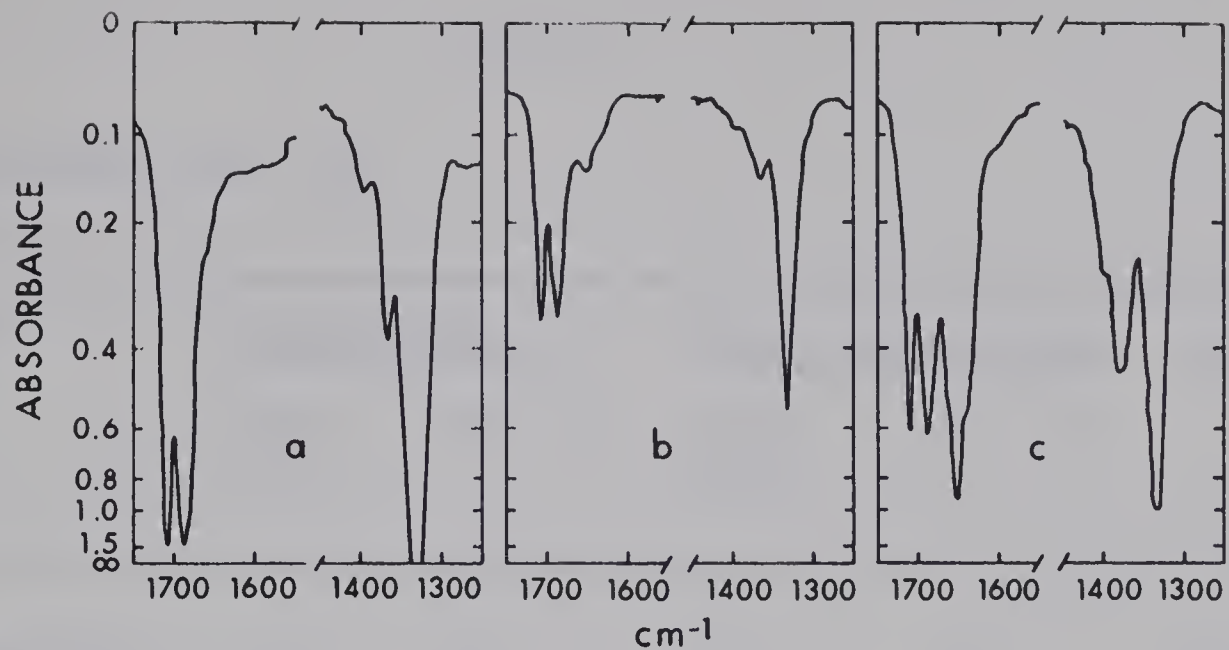


Figure 12. Infrared spectra for trimethyltin dichloroacetate in carbon tetrachloride: a, 2.8 mg/ml, 5.0 mm cell; b, 11 mg/ml, 0.5 mm cell; c, 18 mg/ml, 0.1 mm cell.

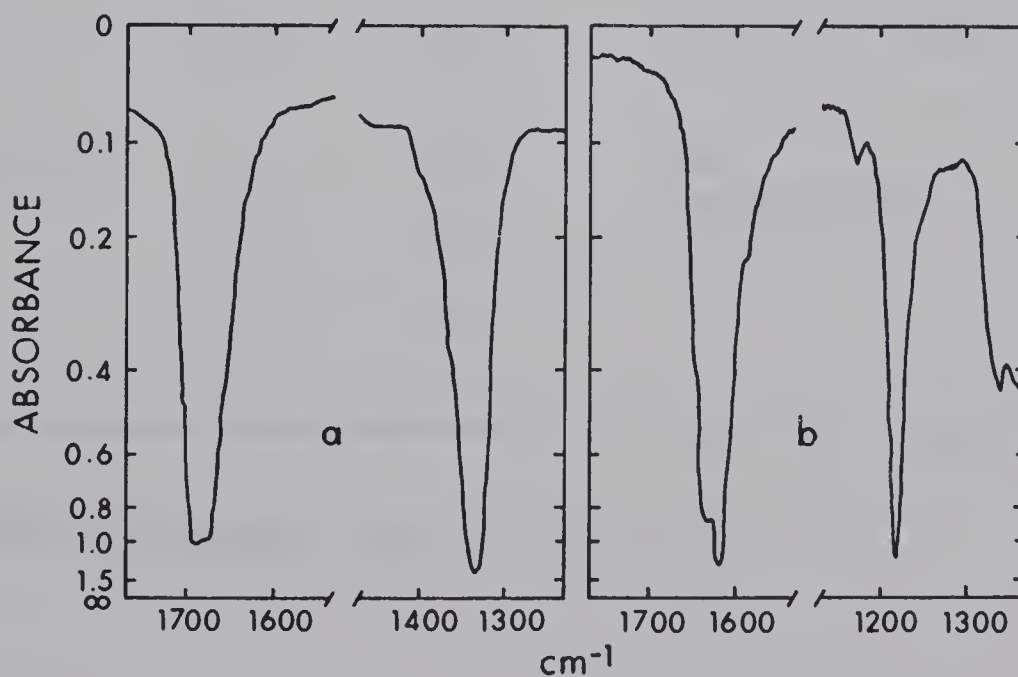


Figure 13. Infrared spectra of trimethyltin dichloroacetate: a, 17 mg/ml in CHCl₃, 0.5 mm cell; b, Mull in halocarbon oil.

TABLE IX

MOLECULAR WEIGHT DATA (a)

Compound	<u>Dibromomethane</u>		<u>Carbon Tetrachloride</u>		Calcd.
	Concn. mg/ml	Mol. Wt.	Concn. mg/ml	Mol. Wt.	
$\text{ClCH}_2\text{COOSn}(\text{CH}_3)_3$	9.3	272	4.3	296	257
	14.2	266	8.9	300	
	20.0	270			
$\text{Cl}_2\text{CHCOOSn}(\text{CH}_3)_3$	8.6	307	3.8	315	292
	16.8	299	7.0	302	
	26.8	301	11.0	328	
$\text{Cl}_3\text{CCOOSn}(\text{CH}_3)_3$	11.1	359	Not sufficiently soluble		326
	16.5	329			
	25.2	320			

(a) Mechrolab Osmometer, benzil calibration, 37°.

1368 cm^{-1} bands are assigned as the asymmetric and symmetric carbon-oxygen stretching modes of the dichloroacetate group in bridging position between two tin atoms. These values differ from the values 1570 and 1420 cm^{-1} found in unsubstituted trialkyltin acetates (25, 26, 42), and a similar trend is observed in the sodium salts of the corresponding acids (26).

The $1708\text{-}1687\text{ cm}^{-1}$ doublet and the 1330 cm^{-1} band (Figure 12) are identified with the unassociated form of trimethyltin dichloroacetate. The occurrence of a doublet requires comment, and is considered to be due to the presence of two conformational isomers of the molecule. Cummins (43) and Vilarem and Maire (44) have explained in this way their observations on tributyltin haloacetate esters, in which doublets with similar separation occur. Two possible conformations are shown in Newman projections as (XIII, cis) and (XIV, gauche).

In chloroform solution (Figure 13a), trimethyltin dichloroacetate exhibits two broad bands at 1680 cm^{-1} and 1330 cm^{-1} , and there is very little change with concentration. Again, the broadening of carbonyl bands in chloroform, as occurs in metal carbonyl spectra (34) presumably obscures the detail visible in carbon tetrachloride. Indistinct shoulders around the 1660 cm^{-1} and 1370 cm^{-1} may be due to a low concentration of an associated form.

In the solid state (Halo-oil mull, Figure 13b), the dichloroacetate shows strong bands at 1620 and 1380 cm^{-1} , with definite shoulders at 1650 and 1635 cm^{-1} . Similar bands have been observed by other workers (6). The general position suggests they are due to a bridging dichloroacetate group of some type, and the multiplicity of bands may again be due to a conformational effect.

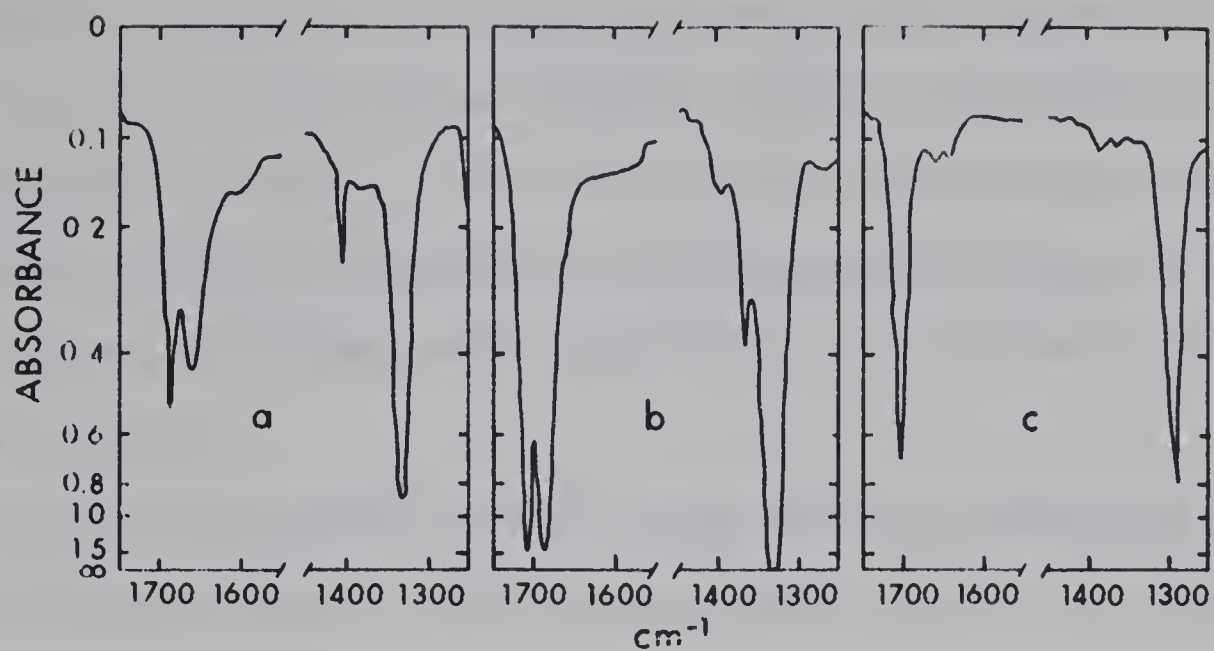
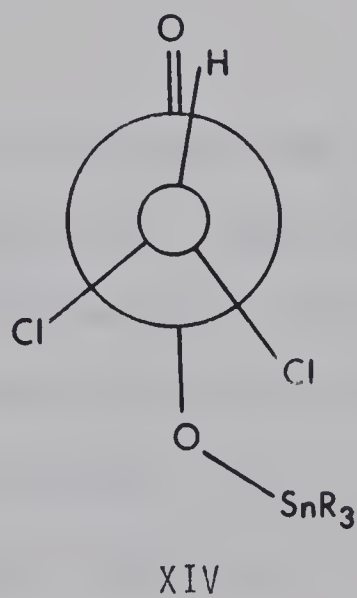
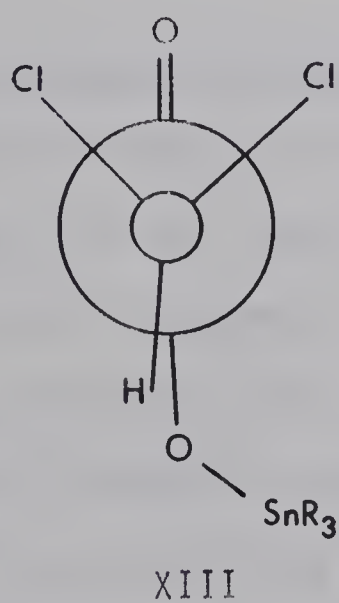


Figure 14. Infrared spectra in carbon tetrachloride: a, trimethyltin monochloroacetate; b, trimethyltin dichloroacetate; c, trimethyltin trichloroacetate.



Spectra of mono-, di- and tri-chloroacetates are compared in Figure 14, in the carbon-oxygen stretching region, and probable assignments are given in Table X. The doublet due to conformational effects is of course lacking in trimethyltin trichloroacetate (Figure 14 c). The assignments are in reasonable accord with those of others which have been reported.

The possibility should be born in mind that the carboxylate group could be bidentate (and the tin five-coordinate) even in the absence of association if chelation is invoked. However, the concentration dependence observed in carbon tetrachloride would only be expected for an equilibrium involving association. The presence of small amounts of chelate monomer cannot be ruled out entirely on the basis of present findings.

Tin-Carbon Stretching Region.

The three chloroacetate derivatives show bands near 546 cm^{-1} (strong) and 512 cm^{-1} (weak) in chloroform solution. These bands can be assigned with reasonable confidence to the asymmetric and symmetric tin-carbon stretching modes respectively. The presence of presumably tetrahedral trimethyltin groups is thus established. This is consistent with the non-bridging chloroacetate groups indicated by the carbonyl-carboxyl region of the spectrum.

Complex Formation Studies.

Increasing amounts of pyridine added to a chloroform solution of trimethyltin dichloroacetate eliminated the 512 cm^{-1} band, presumably by making the tin atom five-coordinate with planar SnC_3 group. This confirms the identity of the 512 cm^{-1} band, and is entirely comparable with the results obtained in the trimethyltin formate-pyridine system.

TABLE X

CARBONYL-CARBOXYL ASSIGNMENTS IN TRIALKYLTIN ACETATES AND
CHLOROACETATES

Compound	Solvent (a)	Free, ester-like		Associated, bridging	
		v(CO) asym.	v(CO) sym.	v(CO) asym.	v(CO) sym.
$\text{CH}_3\text{COOSn}(\text{CH}_3)_3$	CHCl_3 Nujol	1658	1318	1570	1425 (f)
$\text{CH}_3\text{COOSn}(\text{C}_2\text{H}_5)_3$	CCl_4 Nujol	1655	1302	1572	1412 (25)
$\text{ClCH}_2\text{COOSn}(\text{CH}_3)_3$	CCl_4 Halo oil	1688-1660(b)	1333	1615	1378 (f)
$\text{ClCH}_2\text{COOSn}(\text{C}_4\text{H}_9)_3$	CCl_4 (?)	1688-1661(b)		1596	1404 (26)
$\text{Cl}_2\text{CHOOSn}(\text{CH}_3)_3$	CCl_4 Halo oil	1708-1687(b)	1330	1652 1620(c)	1368 (f)
$\text{Cl}_2\text{CHOOSn}(\text{C}_4\text{H}_9)_3$	CCl_4 (?)	1698-1679(b)		1627	1364 (26)
$\text{Cl}_3\text{COOSn}(\text{CH}_3)_3$	CCl_4 CHCl_3 Nujol	1704 1702	1290 1305	1648(d)	1348 (f)
$\text{Cl}_3\text{COOSn}(\text{C}_4\text{H}_9)_3$	CCl_4 (?)	1705		1646	1340 (26)

(a) Solid when in nujol, halo oil and (?).

(b) Doublet due to conformational effect, cf. text.

(c) With shoulders at 1650 and 1635 cm^{-1} .

(d) Shoulder at 1662 cm^{-1} .

(e) With sharp weaker band at 1400 cm^{-1} .

(f) This work.

NMR Spectra.

As a result of the general misconception that trimethyltinchloroacetates are insoluble, no previous investigation of this kind has been carried out. Complete NMR data for the three trimethyltin chloroacetates are given in Table XI. The most significant factor revealed in studying the coupling constants of these three compounds is the fact that in chloroform solutions from -30° to $+50^{\circ}\text{C}$ J values for all three compounds are close to 59 cps. This is close to the value for trimethyltin chloride (58.5 cps), and suggests that the molecules are essentially unassociated, with four-coordinate tin. In an earlier interpretation of this result (45) it was assumed that the five-coordinate species present was similar to that postulated for trimethyltin formate and trimethyltin acetate where J approaches the limiting value of 70 cps. Little five-coordinate tin was believed present because of J nearly equal the four-coordinate value ≈ 59 cps.

In view of the discussion of the trimethyltin pivalate case above, an alternative explanation must now be considered, namely, that the five-coordinate species present is of a special type with a long "bond" bridging carbonyl group, the J value of which is essentially identical to that of four-coordinate tin. It should be noted, however, that the weighted value of J is not a very sensitive measure of association since a 5% change in the population of the four- and normal five-coordinate states would change J by only about 0.5 cps.

A single NMR measurement on a carbon tetrachloride solution of trimethyltin dichloroacetate (approximately 30 mg/ml, 33.5°C) showed $J=61.4$ cps, a value which implies 20-25% of the tin is normal five-coordinate in this solvent under these conditions. This behavior is

TABLE XI

PROTON MAGNETIC PARAMETERS FOR TRIMETHYLTIN CHLOROACETATES (a)

Solvent	Temp.	R = (CH ₃) ₃					
		ClCH ₂ COOSnR(b)		Cl ₂ CHCOOSnR(c)		Cl ₃ CCOOSnR(d)	
		J ₁ cps	J ₂	J ₁ cps	J ₂	J ₁ cps	J ₂
	°C						
CDCl ₃	50	58.8	58.7	56.2			
CDCl ₃	33.5	58.9	56.4	59.6	56.9	59.0	56.5
CDCl ₃	0	59.3	56.7	59.3	56.4	59.6	56.9
CDCl ₃	-30	59.0					
CDCl ₃ /C ₅ D ₅ N	50	67.4	64.4	68.2	65.2		
CDCl ₃ /C ₅ D ₅ N	33.5	67.9	64.8	68.3	65.3	68.3	65.2
CDCl ₃ /C ₅ D ₅ N	-10	68.1	65.1	68.4	65.3	68.3	65.3

(a) Solutions saturated at room temperature. Coupling constants in cps; J₁=J(¹¹⁹Sn-CH₃); J₂=J(¹¹⁷Sn-CH₃). γ values for CDCl₃ solutions.

(b) (CH₃)₃Sn at γ9.39, ClCH₂ at γ5.83.

(c) (CH₃)₃Sn at γ9.33, Cl₂CH at γ4.13.

(d) (CH₃)₃Sn at γ9.28.

in apparent contradiction with the infrared spectra discussed previously. Judging from the intensity of the carbonyl stretching bands (Figure 12 c), it is reasonable to assume that the concentration of bridging species present in the NMR study is much greater than the J value indicates. Clarification of the apparent contradiction may be found in the unsymmetrically bridged associated form with a J value nearly equal to that of the monomeric four-coordinate form, or in the possibility of chelation contributing to the intensity of the bridged carbonyl band. Apparently chloroform tends to reduce the degree of association of the trimethyltin carboxylates to a greater extent than carbon tetrachloride.

Complex Formation Studies.

As is apparent from the last three entries for each compound in Table XI, addition of excess pyridine increases J to values in the usual five-coordinate range. The value for all three compounds at 33.5°C is close to 68 cps, slightly greater than the 65.8 cps observed for trimethyltin acetate or the value of 66.1 cps observed for trimethyltin pivalate. The slightly larger value observed for the chloroacetates is very likely due to the higher electron withdrawing ability of the chloroacetate ligands, which increases the acceptor ability of the tin atom, and thus stabilizes the pyridine adduct.

EXPERIMENTAL

Trimethyltin Hydroxide.

The method of Luitjen (46) was used with modification. A solution of sodium hydroxide (3.2 g, 10 ml water) was slowly added to a magnetically stirred solution of 15.95 g (0.08 mole) of trimethyltin chloride in 10 ml of water. After stirring \approx 2 hours the precipitate formed was isolated by filtration with suction using a sintered glass funnel. The filter cake was dried in a dessicator \approx 12 hours, transferred to a soxhlet extractor and continuously extracted with hot petroleum ether (Skelly B) for about 6 hours. The extract, after filtration and evaporation, left a white semi-solid that formed a hard mass on adding a few drops of water. Pulverizing, drying and subliming at high vacuum provided the pure product. M.P. 118-120°C [Sealed Capillary] Lit. (46) 118-119°C.

Heating during sublimation was found to result in the formation of tetramethyltin (NMR) and a white non-volatile solid, presumably dimethyltin oxide, confirming the results of Kraus and Bullard (47) on the thermal stability of trimethyltin hydroxide.

Trimethyltin Formate (Insoluble).

Formic acid (7 ml 98%) was added to 2.03 g (0.011 mole) of trimethyltin hydroxide and the mixture stirred magnetically. Heat was evolved, the solution turned light yellow and ultimately a clear deep blue purple with no solid present. Excess formic acid was removed with a rotary evaporator followed by room temperature high vacuum. High vacuum sublimation (\approx 3 microns) at 60-70°C yielded the pure product. M.P. 147-148°C (Gallenkamp) Lit. (6) 151°C. The material was

insoluble in chloroform and cyclohexane.

Trimethyltin Formate (Soluble).

A. High Pressure CO Conversion

Insoluble trimethyltin formate (0.6597 g) and cyclohexane (10 ml) in a 50 ml round bottom flask were placed in a clean 300 ml Magnedash autoclave. The autoclave was pressurized to 3000 psi at room temperature with carbon monoxide and heated ($\approx 95^{\circ}\text{C}$) for 24 hours. The autoclave was allowed to cool, the pressure released and the autoclave opened to reveal fine white needle crystals present on the closing plate of the autoclave, a large mass of white needles and clear liquid in the flask and clear liquid in the bottom of the autoclave.

Infrared examination of the cyclohexane showed strong absorptions in the carbonyl region. The cyclohexane was decanted from the solid in the flask and the solid dried to yield 0.535 g of trimethyltin formate, completely soluble in chloroform. The analytical sample was prepared by recrystallization from chloroform/pentane, followed by sublimation; after sublimation, the material was still soluble. [Found: C, 22.95, 23.21; H, 4.55, 4.85; O, 15.54, 15.53; $\text{C}_4\text{H}_{10}\text{O}_2\text{Sn}$. Calcd: C, 23.01; H, 4.79; O, 15.33%.] Molecular weight calcd: 208.7; found: 768 (3.610 mg/835.6 mg CCl_4); 775 (17.025 mg/1076 mg CH_2Br_2); 730 (8.880 mg/1601.3 mg CH_2Br_2); 320 (4.602 mg/ml Benzene); 212 (1.300 mg/211.3 mg ethanol). M.P. softening beginning at 135°C , liquification complete near 148°C (sealed capillary, Gallenkamp apparatus). Observed microscopically on a Kofler hot stage, the behavior was extremely complex, with sublimation and several apparent phase changes beginning around 100°C .

B. Sealed Tube Conversion.

A small quantity (≈ 0.1 g) of insoluble trimethyltin formate was placed in a pyrex glass tube, cyclohexane (10 ml) added, the tube cooled in liquid nitrogen and sealed. A clear colorless solution was obtained after 12 hours heating in an oven at 90-100°C. The long, thin, white needles which formed on cooling (≈ 0.08 g) were identical (IR and NMR) to those prepared under high pressure.

Additional preparations were successfully carried out using either a steam bath or oven at $\approx 140^\circ\text{C}$.

Trimethyltin Acetate (Insoluble).

Glacial acetic acid was added dropwise to an aqueous solution of freshly sublimed trimethyltin hydroxide until no additional fine, white needles formed. The mixture was filtered and the solid dried in a vacuum dessicator. Following recrystallization from hot petroleum ether (Skelly B) the compound melted at 194-195°C (sealed capillary, Gallenkamp) and 198.5-200°C (Kofler hot stage). Lit. (33) 196.5-197.5°C.

Trimethyltin Acetate (Soluble).

A. High Pressure CO Conversion.

Trimethyltin acetate (insoluble, 0.29 g) and cyclohexane (≈ 10 ml) were placed in a 50 ml 14/20 round bottom flask and the flask placed in a 500 ml Parr rocking autoclave. The autoclave was pressurized to 2000 psi at room temperature with carbon monoxide and heated to 80°C. After heating 26 hours the autoclave was cooled, the pressure released and the vessel opened to reveal long, fine, white needles on the closing plate, a large mass of needle clusters and a small amount of cyclo-

hexane in the flask and clear liquid in the bottom of the pressure vessel.

Infrared examination of the cyclohexane mother liquor showed strong absorptions in the carbonyl region. The cyclohexane was decanted from the solid and the solid air dried to yield 0.26 g of trimethyltin acetate. [Found: C, 26.68; H, 5.25; O, 13.26 Calcd: C, 26.96; H, 5.39; O, 14.37%.] Molecular weight calcd: 222.7; found: 252, (9.977 mg/ml CH_2Br_2); 211 (10.950 mg/ml ethanol). The melting point observed microscopically on a Kofler hot stage using a sealed capillary was very complex. Sublimation began about 110°C with many small short needles being formed. Many apparent phase changes occurred between 110-170°C with large clear crystals forming. Liquification beginning at 205°C with apparent evaporation and new crystal formation; very sudden and complete liquification at 213°C.

Trimethyltin Acetate (Soluble).

B. Sealed Tube Conversion.

A small quantity of insoluble trimethyltin acetate and ≈ 10 ml of cyclohexane were put into a glass tube, cooled in liquid nitrogen and the tube sealed. A clear colorless solution was present after ≈ 12 hours heating in a steam bath. On cooling, long, fine white needles formed. The crystals were removed by filtration and air dried. NMR and IR spectra of chloroform solutions were identical to those obtained of the high pressure converted material. Melting was sharp at 191-192°C in a sealed capillary (Gallenkamp apparatus).

Trimethyltin Pivalate.

Excess pivalic acid (Eastman white label) was added to an aqueous solution of trimethyltin hydroxide and the mixture stirred about one half hour. The white solid which formed was filtered and recrystallized (CHCl_3 -pentane-ether) at -80°C . The recrystallized compound was washed once with -80°C ether and air dried. M.P. $151-152^\circ\text{C}$ with considerable sweating prior to melting.

The analytical sample was further purified by recrystallization (hexane/ether) and room temperature high vacuum sublimation. [Found: C, 36.13; H, 6.58; O, 12.06; $\text{C}_8\text{H}_{18}\text{O}_2\text{Sn}$ Calcd: C, 36.29; H, 6.80; O, 12.08%.] Molecular weight calcd: 264.8; found: 344 (7.491 mg/ml Benzene); 351 (8.717 mg/ml CH_2Br_2); 236 (6.751 mg/ml ethanol). M.P. $139-140^\circ\text{C}$ (Gallenkamp apparatus, sealed capillary).

Trimethyltin monochloroacetate.

Monochloroacetic acid (1.0 g) dissolved in a small quantity (≈ 10 ml) of water was added to a magnetically stirred aqueous solution of trimethyltin hydroxide (1.4 g in ≈ 10 ml water). No solid formed within 30 minutes. Evaporation of the clear colorless solution on a steam bath produced white needle crystals. High vacuum sublimation at room temperature produced a small amount of unreacted acid, M.P. $50-55^\circ\text{C}$. Continued high vacuum sublimation at 70°C produced a white crystalline sublimate, M.P. $140-143^\circ\text{C}$ (Gallenkamp apparatus, sealed capillary). Resublimation (80°C , ≈ 5 mm Hg) produced the pure compound. [Found: C, 22.50; H, 4.14; O, 12.26; Cl, 13.53 $\text{C}_5\text{H}_{11}\text{O}_2\text{ClSn}$ Calcd: C, 23.35; H, 4.28; O, 12.44; Cl, 13.79%.] Molecular weight calcd: 257; found: 272 (9.29 mg/ml CH_2Br_2); 266 (14.205 mg/ml CH_2Br_2); 270 (20.055 mg/ml CH_2Br_2); 296 (4.268 mg/ml CCl_4); 300 (8.933 mg/ml

CCl_4). M.P. 143-145°C (Gallenkamp apparatus, sealed capillary)
Lit. (6) 148°C.

Trimethyltin dichloroacetate.

Dichloroacetic acid (0.91 g, 7 mmole) dissolved in water (10 ml) was added to a water solution of trimethyltin hydroxide (1.268 g, 7 mmole). The clear, colorless solution was stirred approximately 15 minutes at room temperature. No precipitate formed. The solution was poured into a 10 cm petri dish and evaporated to dryness on a steam bath. The resulting white solid residue was dried overnight in a calcium chloride dessicator and sublimed twice in high vacuum. Yield 1.184 g white needles. [Found: C, 20.61; H, 3.40; O, 10.78; Cl, 24.31 $\text{C}_5\text{H}_{10}\text{O}_2\text{Cl}_2\text{Sn}$ Calcd: C, 20.59; H, 3.43; O, 10.97; Cl, 24.32%.] Molecular weight calcd: 291.6; found: 307 (8.662 mg/ml CH_2Br_2), 299 (16.840 mg/ml CH_2Br_2), 301 (26.842 mg/ml CH_2Br_2), 315 (3.783 mg/ml CCl_4), 302 (7.013 mg/ml CCl_4), 328 (10.980 mg/ml CCl_4). M.P. 138-140°C (Kofler apparatus, cemented microscopic slide), 134-135°C (Gallenkamp apparatus, sealed capillary), Lit. (6) 135°C.

Trimethyltin trichloroacetate.

Trichloroacetic acid (0.838 g, 5.1 mmole) was added to a water-ether solution of trimethyltin hydroxide (1.033 g, 5.7 mmole). The mixture was shaken approximately five minutes, poured into a 10 cm petri dish and evaporated to dryness on a steam bath. The resulting shiny white flakes were dried overnight in a calcium chloride dessicator and sublimed thermally (110°C) onto a water cooled condenser. [Found: C, 18.40; H, 2.90; O, 4.83; Cl, 32.45 $\text{C}_5\text{H}_9\text{O}_2\text{Cl}_3\text{Sn}$ Calcd: C, 18.42; H, 2.76; O, 9.81; Cl, 32.62%.] Molecular weight calcd:

326.1; found: 359 (11.118 mg/ml CH_2Br_2), 329 (16.521 mg/ml CH_2Br_2), 320 (25.226 mg/ml CH_2Br_2). M.P. 176-184°C with apparent decomposition (Kofler apparatus, cemented microscopic slide), 175-176°C (Gallenkamp apparatus, sealed capillary), Lit. (6) 179°C.

CHAPTER III

DIMETHYLTIN DICARBOXYLATES

Dialkyltin dicarboxylates were described by Cahours (48) in 1860. and various derivatives have been studied by Harada and co-workers (49, 50). No study limited to dimethyltin dicarboxylates has been reported; however, dimethyltin diformate has been studied in the solid state by infrared techniques. This chapter deals with ten dimethyltin dicarboxylates evenly divided into two groups. The first group of five contain aliphatic carboxylic acid, i.e., formate, acetate, propionate, isobutyrate and pivalate (2,2-dimethylpropionate); the remaining group contains halogen-substituted aliphatic carboxylic acids, (mono-, di- and tri-chloroacetate, monobromoacetate, 2-chloro-2-methyl propionate). In view of the nature of this study the two groups will be discussed separately, beginning with the simple aliphatic carboxylic acids.

ALIPHATIC DICARBOXYLATES

Based on the similarity of solid state infrared spectra of dimethyltin diformate and sodium formate, Okawara, Webster and Rochow (6) suggested the compound exists as an ionic solid composed of dimethyltin cations and formate anions. The dimethyltin cation was believed to be linear due to the presence of a single tin-carbon stretching band. The ionic nature was considered to explain the insolubility in organic solvents. Subsequently, it was suggested (7) the dicarboxylates are not ionic solids but infinite chain polymers composed of linear dimethyltin groups symmetrically bridged by car-

boxylate groups. The compound may be viewed as a chain of octahedra with four oxygens in the equatorial plane with the tin atom, and the methyl groups axially trans. Six-coordinate tin is an essential feature of such a structure.

Very recently (35) dimethyltin diacetate has been prepared and reported to be readily soluble and monomeric in organic solvents. It is reported to be very easily hydrolyzed by atmospheric moisture forming the symmetrical tetramethyl-1,3-diacetoxy distannoxane.

As discussed briefly in the preceeding chapter, it has been suggested by Okawara et. al. (35) that dimethyltin diacetate exists as an octahedron with "bidentate acetate groups with non-equivalent covalency in the Sn-O bonds" and a dimethyltin moiety "which may well be non-linear." In view of the rather unusual structure postulated it is desirable to examine fully the experimental evidence which led to this postulate.

Cryoscopic molecular weight determinations in benzene indicated essentially monomeric behavior [Found: 269, 277 at 2.68 and 5.84% w(sample)/w(benzene), respectively: $C_6H_{12}O_4Sn$, Calcd: 266.9.] Initially, the slightly higher value at increased concentration was ignored as the infrared data (vide infra) did not support the presence of any polymeric, presumably symmetrically bridged material.

IR band positions were initially reported (35) as being essentially the same in the molten liquid at 85°C [M.P. 67°C], in a crystalline film at room temperature and in approximately 20% CCl_4 solution. The -COO- stretching vibration bands (1607 cm^{-1} , COO asymmetric; 1380 cm^{-1} , COO symmetric; in CCl_4) were similar to those of other monomeric dialkyltin diacetates which have been reported to contain

chelating carboxyl groups (51).

A more detailed publication (52) disclosed the presence of an additional strong asymmetric CO_2 stretching vibration at about 1565 cm^{-1} in the solid state and as a neat liquid. Also, an increase in intensity of the bands at $1400\text{--}1440\text{ cm}^{-1}$ was observed, however the 1565 cm^{-1} band was absent in the spectrum of a 7% solution in cyclohexane. The presence of the additional carbonyl stretching band and its similarity in frequency to bands found in trialkyltin acetates has subsequently been attributed to the presence of polymeric, presumably symmetrically bridged material (52).

The suggestion that the tin oxygen bonds are not equivalent in covalent character is based on the fact that the asymmetric stretching band is higher and the symmetric stretching band is lower than those of the trialkyltin carboxylates which have been reported to contain bridging carboxyl groups. In addition, the magnitude of the spin-spin coupling constant J ($82.5\text{ cps}/20\%\text{ CCl}_4\text{ solution}$; $81.7\text{ cps}/\text{neat liquid } 85^\circ\text{C}$) was believed to suggest a non-linear C-Sn-C skeleton with approximately 40% s-character in the Sn-C bonds.

As was discussed in the preceeding chapter a structure with non-equivalent covalency in the tin oxygen bonds raises several interesting questions, i.e., isolated canonical resonance forms, etc., and will not be repeated here.

NMR has only recently (52) been used to help determine the structure of dimethyltin dicarboxylates. In addition to providing information regarding the number and type of protons present which can confirm or question analytical data and provide important information regarding impurities, the observation of spin-spin coupling

constants can yield information concerning the geometry about the tin atom. Most workers have interpreted their spin-spin coupling constant (J) data in terms of the coordination state of the tin atom (19) and the distribution of s-character among the various atoms bonded to tin. Distribution of s-character in turn has been used to suggest the hybridization of the tin orbitals. Some aspects of this use of coupling constant data have been questioned very recently by Kitching (53); therefore detailed discussion relating to the magnitude of J and its structural implications is deferred until all five aliphatic dicarboxylates have been discussed in general terms.

RESULTS AND DISCUSSION

Dimethyltin diformate.

Dimethyltin diformate has been reported (6) to be insoluble, consequently data concerning the properties of the compound in solution are lacking. The compound prepared in this study is sufficiently soluble, as prepared, to permit the use of solution infrared and NMR spectroscopy as well as molecular weight determination in solution.

Molecular Weight Studies.

A single molecular wieght determination in dibromomethane indicates that the compound is associated in solution; the degree of association (3.8) is similar to that observed with soluble trimethyltin formate. It is assumed that a large number of species may be present but that the weighted average may be approximated as a mixture of trimeric and tetrameric species.

Infrared Spectra.

Complete infrared data are given in Table XII. Solid state and solution spectra in the regions of interest are illustrated in Figures 15, 16 and 17 .

Carbonyl-Carboxyl Region.

Two distinct carbonyl absorptions in the solid state (1655 and 1575 cm^{-1} /Nujol; 1645 and 1570 cm^{-1} /KBr) seem to indicate both ester-like and bridging carboxylate groups are present in the molecule. As might be expected the lower frequency band is more intense. The frequency of this band is essentially identical to that observed in trimethyltin formate in the solid state and is similarly assigned to the asymmetric stretching mode of a symmetrically bridged carboxylate group. Similarly, the higher frequency band is assigned to the asymmetric stretching mode of an unassociated formate group. The corresponding symmetrical stretching modes are observed at 1390 and 1365 cm^{-1} /Nujol; $1390-80$ and 1360 cm^{-1} /KBr respectively. Confirmation for assigning the lower frequency asymmetrical band to a bridging carboxylate group is provided by the absence of such a band in a CHCl_3 solution spectrum.

Several additional features of the CHCl_3 solution spectrum require comment. The presence of medium intensity bands at 1750 and 1730 cm^{-1} is puzzling. Free formic acid exhibits a carbonyl absorption in the $1700-1710\text{ cm}^{-1}$ region and is therefore considered unlikely as the source of the observed bands. Some type of aldehyde or ketone would be consistent with the observed frequencies; however, additional studies would be necessary to clarify this problem. Dissolving the solid would be expected to increase the intensity of the "free"

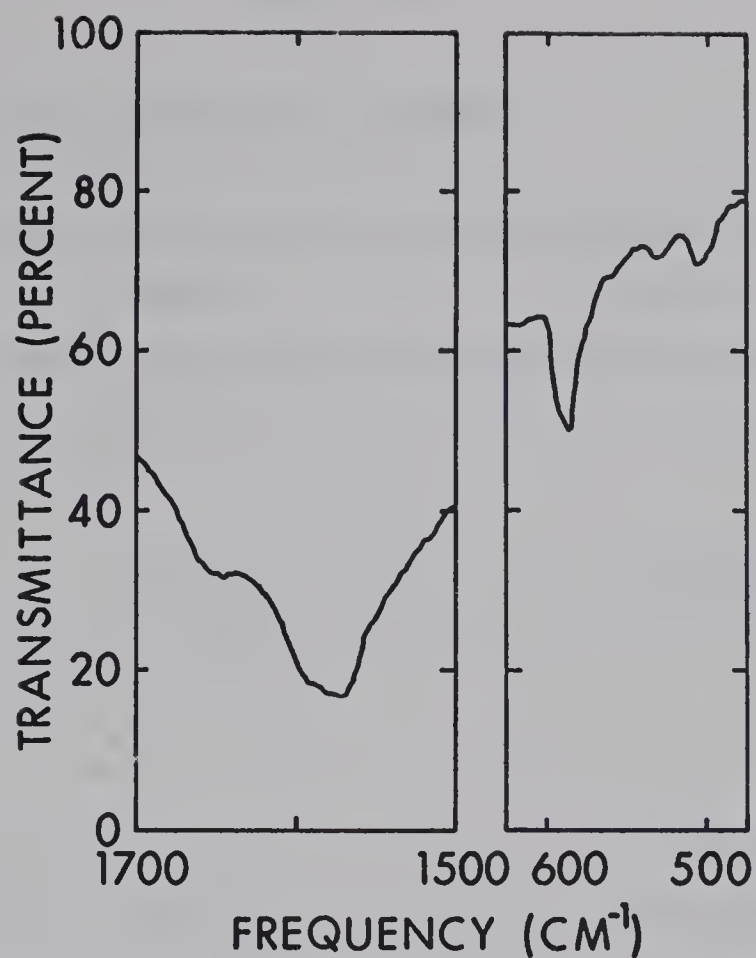


Figure 15. Infrared spectra of dimethyltin diformate, KBr disc.

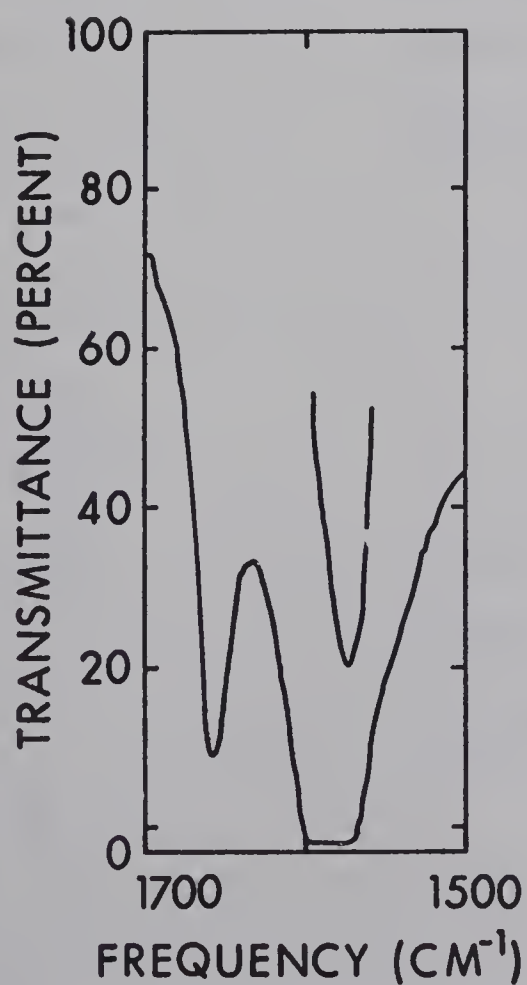


Figure 16.

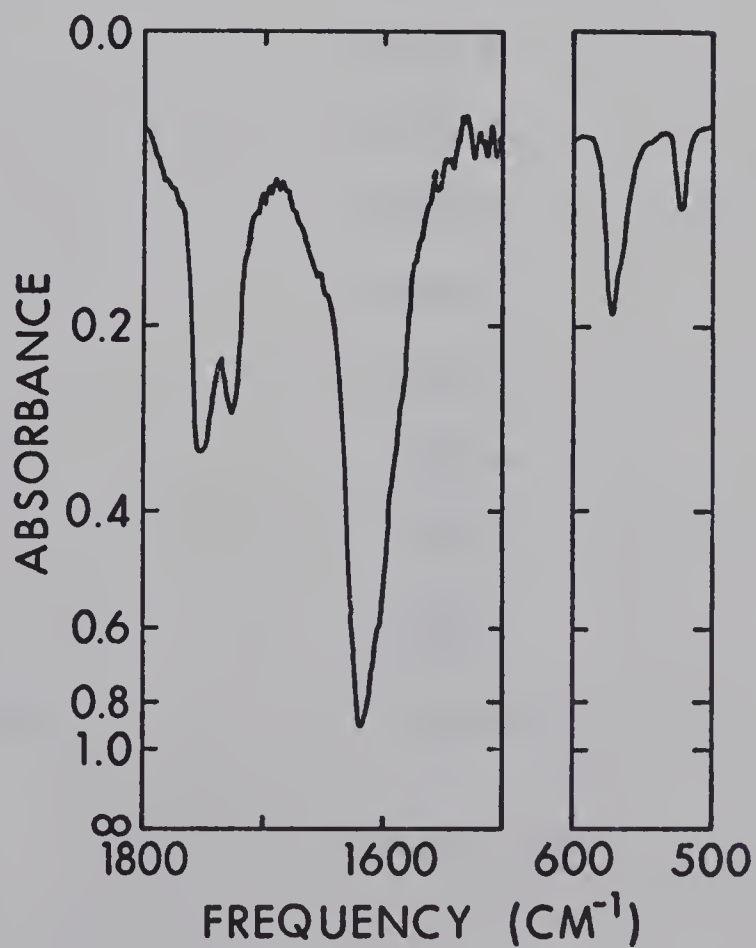


Figure 17.

Figure 16. Infrared spectra of dimethyltin diformate, Nujol mull.
Figure 17. Infrared spectra of dimethyltin diformate, chloroform.

TABLE XII

INFRARED SPECTRA FOR DIMETHYLTIN DIFORMATE

CHCl ₃	Nujol	KBr
1750 m		
1730 m		
	1655 m	1645-1625 s, br
1620 s		
1610 <u>sh</u>		
1602 <u>sh</u>		1600 <u>sh</u>
1592 <u>sh</u>	1575 s	1585-1550 s, br
1368 w-m	1390 m	1390-1380 s
1340 m	1365 m	1360 s
1270 s	1225 w	1222 w
1110 w-m		1200 w
1072 w		1068 w
995 w-m		1060 w
800 w-m	812 w-m	800 m-s
780 w-m	795 m	775 s
625 m	770 m	590 m
570 m	590 w-m	535-524 w
565 <u>sh</u>		
520 w-m		
505 vw		

unassociated ($1645\text{-}1655\text{ cm}^{-1}$) band simultaneous to the disappearance of the $1570\text{-}1575\text{ cm}^{-1}$ bridging band, as was observed with trimethyltin formate. Therefore the absence of a band in the $1640\text{-}1600$ region and the presence of a band $25\text{-}35\text{ cm}^{-1}$ lower is rather unusual. It appears that this band must be assigned to the asymmetric stretching mode of some type of formate group although the structure of the formate group concerned is uncertain. Structural implications of this absorption and similar absorptions present in the solution spectra of the other aliphatic dicarboxylates is deferred until the entire series has been discussed.

Tin-Carbon Stretching Region.

Non-linear geometry is indicated for the C-Sn-C skeleton in CHCl_3 solution as absorptions are observed at 570 and 520 cm^{-1} , assignable to the asymmetric and symmetric tin-carbon stretching modes respectively. Interestingly enough, these absorptions are also observed in the solid state, although shifted to slightly higher frequencies (585 and $535\text{-}25\text{ cm}^{-1}/\text{KBr}$).

NMR Spectra.

Complete NMR data pertaining to dimethyltin diformate are given in Table XIII. Two strong resonances at 8.91τ and 1.62τ in a ratio close to 3:1 and two weak resonances at 9.12τ and 9.40τ are observed in the room temperature CDCl_3 solution spectrum. Assignment of the 8.91τ resonance to CH_3 groups on tin is substantiated by the presence of $\text{H}_3\text{C-Sn}$ coupling satellites symmetrically disposed on each side ($J=81.4\text{ cps}$). In view of the location and intensity of the 1.62τ resonance, it is assigned to the proton of a formate group. The two

TABLE XIII

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTIN DIFORMATE

Solvent	Temp. °C	$\text{CH}_3\text{-Sn}$ τ	J^1 cps	J^2 cps	H-COO τ	
CDCl_3	R.T.	8.91	81.4		1.62	(a)
DMSO	R.T.	9.22	102	97	1.70	(b)
DMSO-d_6	R.T.	9.15	101.3	96.6	1.67	(c)
CHCl_3	+55	8.88	80.2	76.1		(d)*
CHCl_3	R.T.	8.87	79.5	76.6		(e)*
CHCl_3	0	8.87	79.6	76.5		(f)*
CHCl_3	-25	8.87	80.2	76.5		(g)*

(a) Impurities 9.12 and 9.40 τ , Internal TMS, A-60 spectrometer.

(b) Impurity 2.93 τ , External TMS, A-60 spectrometer.

(c) Impurity 3.15 τ , External TMS, A-60 spectrometer, approximately
1 g/ml, $\text{H-}^{13}\text{C}$ = 204 cps.

(d) Impurities 9.05 and 9.09 τ .

(e) Impurities 9.06 and 9.09 τ .

(f) Impurities 9.07 and 9.11 τ .

(g) Impurities 9.09 and 9.12 τ .

* CHCl_3 lock, HA-100 spectrometer.

weak resonances (9.12 τ and 9.40 τ) are clearly due to impurities. Decomposition of dimethyltin diformate could result in the formation of tetramethyldiformoxydistannoxane (vide infra) or less likely a small amount of redistribution product trimethyltin formate (appendix).

Variable temperature studies (100 MHz) indicate little change in the magnitude of J and essentially no change in the chemical shift of the methyl groups bonded to tin over an 80°C temperature range.

Complex Formation Studies.

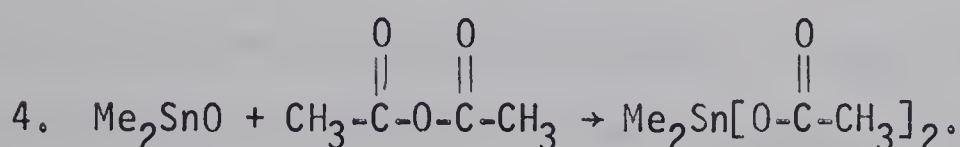
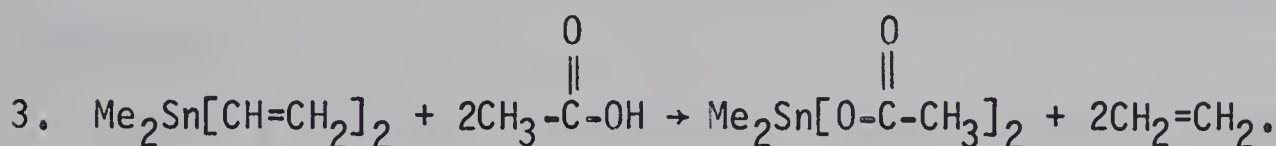
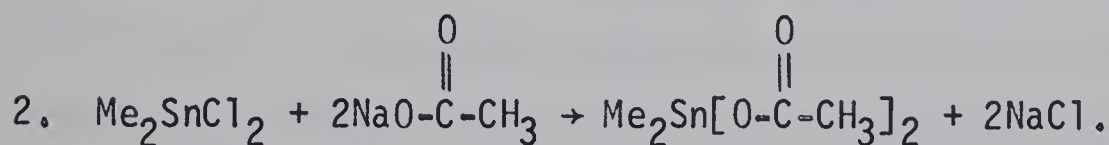
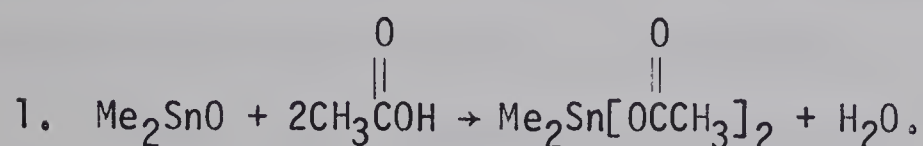
Definite changes in the NMR spectrum occur when DMSO-d₆ is used as solvent. It is well known that this solvent is capable of forming adducts with dimethyltin compounds (30). The observed changes indicate the dimethyltin species present is indeed a complex. Most significantly the coupling constant J has increased to approximately 102 cps and the methyltin resonance has shifted to 9.15 τ . The increase in J and the change in chemical shift of the methyl group on tin are roughly analogous to the changes observed when pyridine was added to trimethyltin carboxylates in CDCl₃ solution. Significantly the formate resonance has not undergone a drastic shift (τ 1.67). Due to the greater solubility of dimethyltin diformate in DMSO, conclusive proof of the assignment of this resonance to a formate was provided by the observation of ¹³C-H coupling J = 204 cps.

Dimethyltin diacetate.

Four different methods of preparation and several purification techniques were used. Completely satisfactory elemental analysis was not achieved; however, satisfactory carbon/hydrogen analysis was obtained on material isolated by vacuum distillation. Extreme

measures were taken to preclude the presence of moisture; however, NMR indicated (vide infra) minor impurities were present but the desired compound was present as the major component. As will be discussed more fully later, the main impurity appears to be the "hydrolysis" product tetramethyl-1,3-diacetoxystannoxane. The apparently extreme sensitivity of this compound to moisture, its reported decomposition during sublimation (54) yet successful vacuum distillation (35) require comment.

Chemical principles indicate at least four methods of preparing dimethyltin diacetate.



Methods 1, 2 and 4 were investigated by Okawara and Rochow (54) who reported "it was impossible to isolate this compound because of decomposition in the course of sublimation or because of polymerization during recrystallization". The only well-characterized product they obtained was tetramethyl-1,3-diacetoxystannoxane.

Each of the methods tried by these workers has been repeated during the course of this research. Numerous procedural variations were tried to no avail. Among the variations used were the following:

All equipment was thoroughly baked at 140°C and cooled under dry nitrogen. Reactions were protected from moisture by CaCl_2 drying tubes and carried out under positive nitrogen pressure. Recrystallizations and/or sublimation manipulations were conducted in a nitrogen filled glove bag dried with P_2O_5 .

Method 1. (a) Excess glacial acetic acid and azeotropic distillation of water with sodium-dried benzene.

(b) Recrystallization using CH_2Cl_2 -pentane in place of methanol.

Method 1, 4. Excess acetic acid with acetic anhydride added to take up any water either formed or present in the acetic acid.

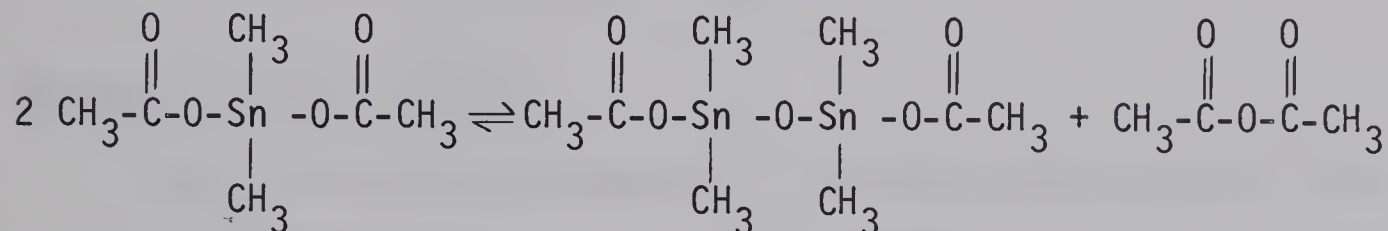
Method 2. Fusion of ingredients in a sealed tube followed by CH_2Cl_2 -pentane recrystallization or sublimation.

Method 3 was tried using glacial acetic acid and a mixture of glacial acetic acid-acetic anhydride followed by recrystallization and/or sublimation. Isolation of pure dimethyltin diacetate proved impossible.

Method 4 followed by vacuum distillation has been reported (35) to yield pure dimethyltin diacetate. Repetition of the available experimental procedure resulted in white, crystalline material which gave satisfactory carbon/hydrogen but low oxygen values on micro-analysis. In spite of the low oxygen value, which could be due to difficulties in analysis, NMR supports the conclusion that the material is indeed dimethyltin diacetate.

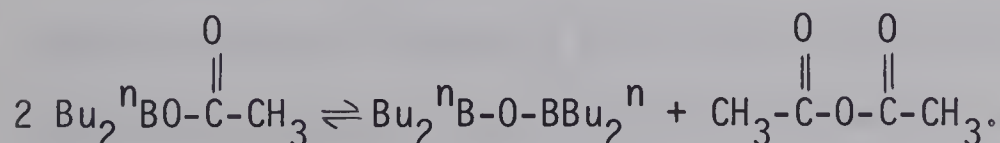
The following hypothesis, although a gross oversimplification, may explain the ease of formation of tetramethyl-1,3-diacetoxy distannoxane from dimethyltin diacetate without the need for water.

If dimethyltin oxide is thought of as the anhydride of dimethylstannoic "acid", i.e. $\text{Me}_2\text{Sn}(\text{OH})_2 \rightarrow \text{Me}_2\text{SnO} + \text{H}_2\text{O}$, dimethyltin diacetate may be thought of as the mixed anhydride of acetic anhydride and the tin anhydride. Condensation of two molecules of this mixed anhydride would produce two new anhydrides, i.e.



Assuming an equilibrium exists in the condensation step, the decomposition during sublimation yet purification during vacuum distillation can be explained. Acetic anhydride present in the solid, being more volatile, is continuously removed during sublimation, thus shifting the equilibrium to the right. Vacuum distillation on the other hand requires liquid materials and the equilibrium is shifted to the left by temperature effects and the intimate contact provided by the liquid state. An analogous situation is found in the initial reaction between the two anhydrides. Reaction is indicated by the disappearance of the dimethyltin oxide when heat is supplied.

Unusual as this hypothesis may seem a somewhat similar situation has been found in some acyloxy derivatives of boron (55). For example, acetyl di-n-butylboronite undergoes disproportion giving an equilibrium between the mixed anhydride and the individual carboxylic and boron acid anhydride. The material is therefore more correctly formulated as the equilibrium mixture.



Relative carbonyl stretching band intensities in the IR spectrum indicate that at room temperature much less than 50% of the boronite is disproportionated (55).

RESULTS AND DISCUSSION

Molecular Weight Studies.

Failure to isolate dimethyltin diacetate which analyzed completely satisfactory precluded the possibility of obtaining meaningful molecular weight data.

Infrared Spectra.

Table XIV lists the IR absorptions observed in solid state and solution spectra of dimethyltin diacetate. Generally, the observations of Okawara, et. al. have been confirmed; therefore the IR discussion will be restricted to variations from the reported absorptions.

Carbonyl-Carboxyl Region.

Nujol mull spectra contain two carbonyl stretching bands at 1614 and 1567 cm^{-1} (Figure 18). These values are slightly higher than those previously reported (52) (1600 and 1560 cm^{-1}) and the difference may be of no real significance. However, cyclohexane solution spectra (Figure 20) contain a very strong absorption of nearly identical frequency 1612 cm^{-1} which appears to indicate the absorption difference is significant. The similarity of frequency in both solid state and solution spectra observed here versus the small change in frequency previously reported may be due to calibration errors in spectrophotometers used but it may also indicate slight differences in

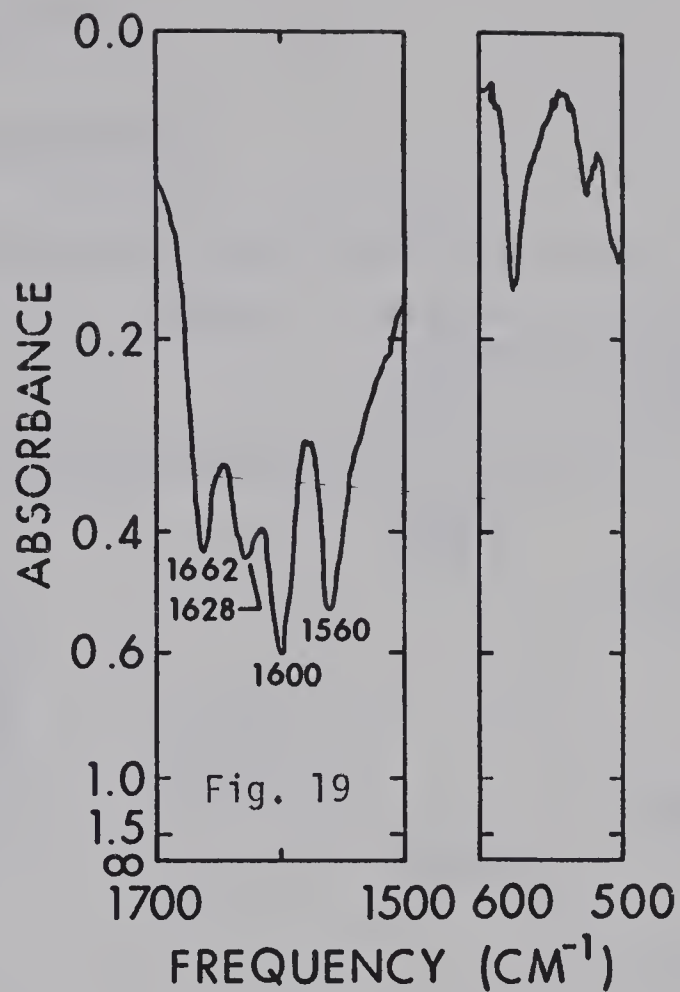
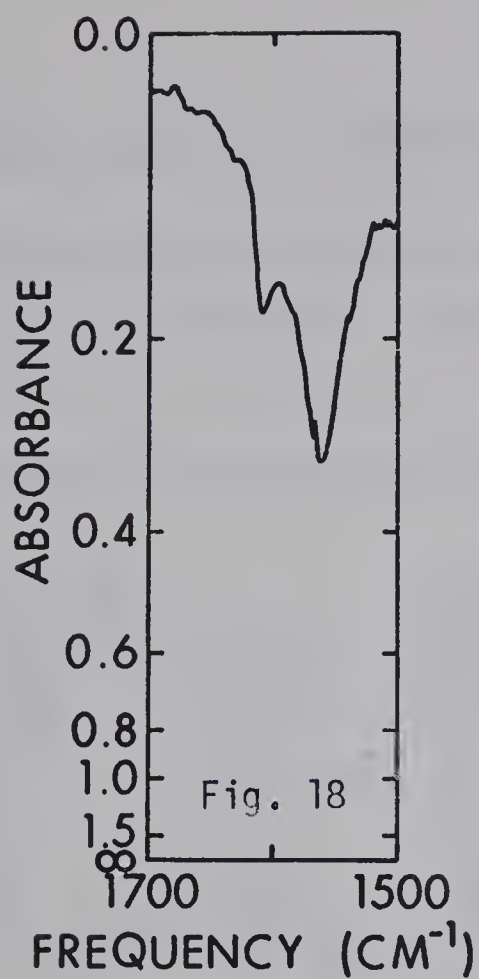


Figure 18. Infrared spectra of dimethyltin diacetate, Nujol mull.
 Figure 19. Infrared spectra of dimethyltin diacetate, chloroform.

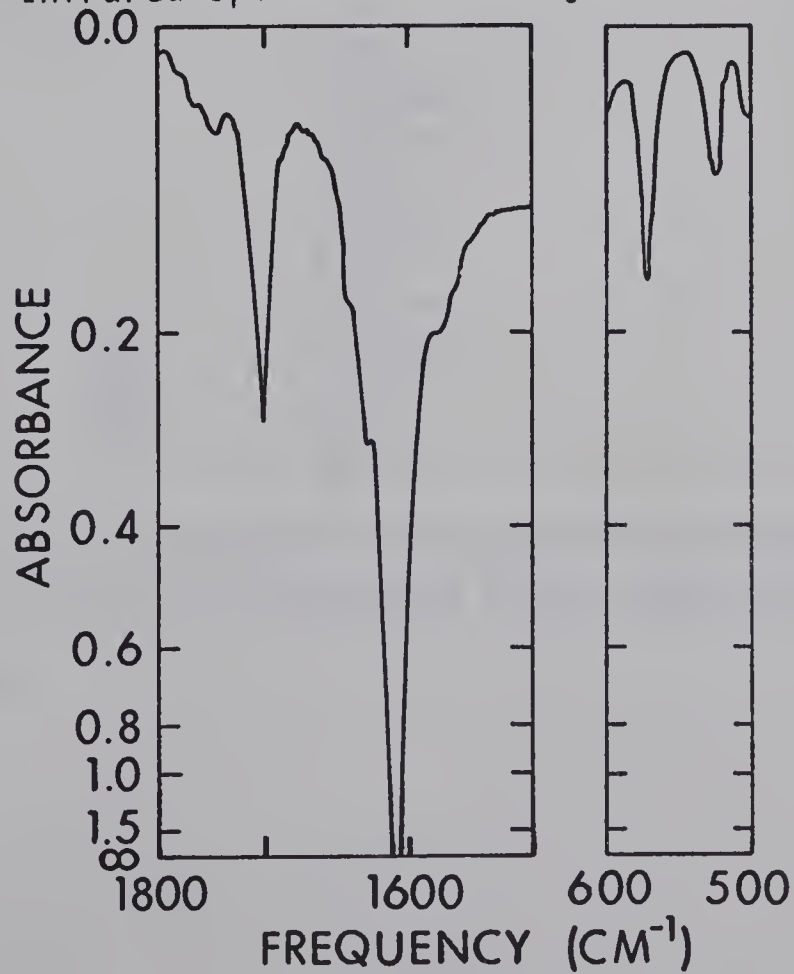


Figure 20. Infrared spectra of dimethyltin diacetate, cyclohexane.

TABLE XIV

INFRARED SPECTRA FOR DIMETHYLTINDIACETATE.

CHCl ₃ *	CHCl ₃ **	C ₆ H ₁₂ *	Nujol	Acetic Anhydride C ₆ H ₁₂	Acetic Acid C ₆ H ₁₂
1750 vw, br		1755 vw		1828 s	
1710 vw, br		1718 m		1760 s	1770 vw
1650 <u>sh</u>	1662 m	1648 <u>sh</u>			1712 vs
1625 <u>sh</u>	1628 m	1633 <u>sh</u>			
1601 <u>vs</u>	1600 s	1612 <u>vs</u>	1614 m		
1560 m	1560 m-s	1575 sh	1567 s		
1400 m		1395 sh			1398 w
1380 s	1376 s	1375 s		1360 m	
1330 s	1328 s	1328 s			
	1318 <u>sh</u>				
		1290 w			1283 m
		1250 w			
				1113 vs	
1048 w		1005 w			
1010 w-m		943 w-m			
945 w		792 w-m, br			
		762 w			
		705 sh			
		698 s			
616 w		622 w-m			
572 m	575	572 w-m			
525 w	525	525 w			
502 w, br	505	505 vw			
490 w, br		490 w			

* Solvents dried with anhydrous Al₂O₃ immediately prior to use.

** 10 mg/ml.

structure in the samples studied. Acetic acid impurity is indicated in the cyclohexane solution by a band at 1718 cm^{-1} . Additionally unassociated and bridged acetate groups are indicated by definite shoulders observed at 1648 and 1575 cm^{-1} respectively.

Chloroform solution spectra (Figure 19) also exhibit bands assignable to unassociated and bridged acetate groups, 1662 and 1560 cm^{-1} as well as the predominant 1600 cm^{-1} carbonyl band.

Tin-Carbon Stretching Region.

Non-linear geometry is indicated in cyclohexane and chloroform solution by the presence of two bands (572 and 525 cm^{-1} /cyclohexane; 572 and 525 cm^{-1} / CHCl_3) assignable as asymmetric and symmetric Sn-C stretching modes respectively.

NMR Spectra.

NMR parameters of dimethyltin diacetate are given in Table XV.

Although contaminated dimethyltin diacetate would ordinarily prove unacceptable for spectroscopic examination, it is considered most valuable in this instance as it provides an opportunity to examine the impurity and determine the effect of adding various reagents.

Figure 21 shows the NMR spectrum of dimethyltin diacetate prepared from Me_2SnO and acetic anhydride with benzene as solvent and purified by recrystallization from CH_2Cl_2 /pentane in a dry nitrogen atmosphere. Two resonances (8.99τ and 7.88τ) assignable to $\text{CH}_3\text{-Sn}$ and $\text{CH}_3\text{-COO}$ respectively, in a ratio of $1.1/1.0$ with $\text{CH}_3\text{-Sn}$ couplings ($J=84\text{ cps}$) associated with the 8.99τ signal would seem to indicate a pure compound; however, elemental analysis was entirely unacceptable.

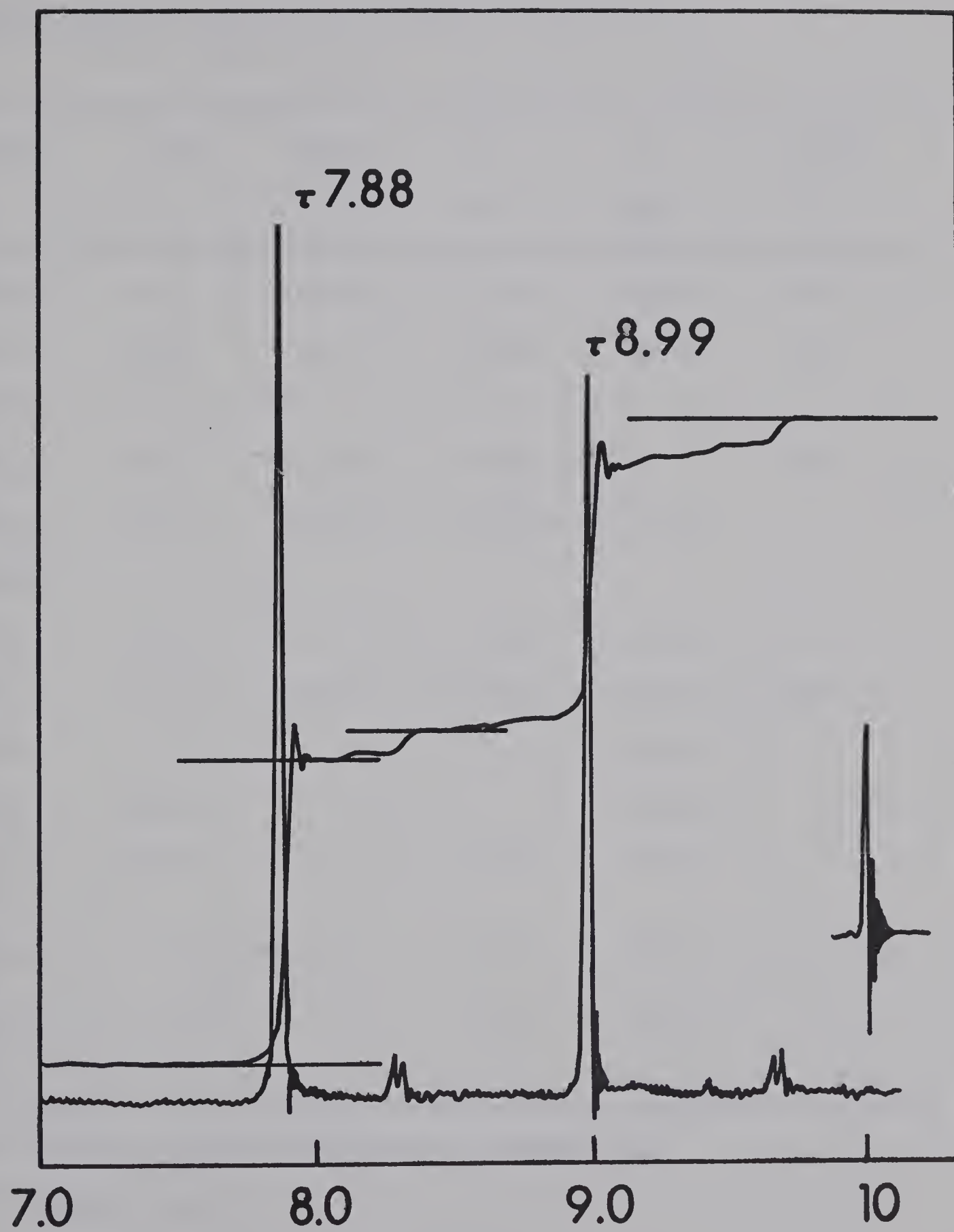


Figure 21. NMR spectrum of dimethyltin diacetate in deuteriochloroform.

TABLE XV

PROTON MAGNETIC PARAMETERS FOR DIMETHYL DIACETATE (a)

Solvent	Temp. °C	$\text{CH}_3\text{-Sn}$ τ	J^1 cps	J^2 cps	CH_3COO τ
CDCl_3	R.T.	8.99	84.0	80.3	7.88
$\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{C}_5\text{D}_5\text{N} \end{array} \right.$	R.T.	9.41	106.5	101.5	8.29
CDCl_3	R.T.	8.98	83.4		7.88 (b)
$\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{CH}_3\text{COOH} \end{array} \right.$	R.T.	8.98	83.6	79.9	
CDCl_3	+55		84.5	80.6	
CDCl_3	41	9.09	85.9	82.8	7.96
CDCl_3	0			86.6	
CDCl_3	-30			87.8	
$\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{D}_2\text{O} \end{array} \right.$	+55		85.2	81.7	
$\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{D}_2\text{O} \end{array} \right.$	41		85.7	82.0	
$\left\{ \begin{array}{l} \text{CDCl}_3 \\ \text{D}_2\text{O} \end{array} \right.$	0		86.7	83.5	

(a) A-60 and A56-60A spectrometers, External TMS.

(b) Impurity 9.13 τ .

Addition of pyridine-d₅ resulted in an increased J (106.5 cps) and a change in the chemical shifts of the methyl groups on tin (9.41 τ) and the acetate methyl (8.29 τ). Attempted purification by sublimation resulted in a material with NMR spectrum as shown in Figure 22a. Decomposition during sublimation is confirmed by the presence of a new resonance at approximately 9.13 τ . The signal appears to be a superposition of two resonances, therefore the value stated is only an approximation.

Elimination of the new resonance by adding excess glacial acetic acid to the sample (Figure 22b) seems to confirm the assignment of this resonance to the "condensation"/"hydrolysis" product tetramethyl-1,3-diacetoxystannoxane.

Variable temperature studies (Table XV) of vacuum distilled material in CDCl₃ support the concept of associated species being present in solution as was pointed out in the infrared spectra discussion. Decreasing temperature should favor some type of associated species and indeed the increased value of J (84.5 cps/+55°C; 89 cps/-50°C) tends to support this assumption.

Ease of hydrolysis has been assumed to be one of the major difficulties encountered in isolating dimethyltin diacetate. Figure 23 illustrated the lack of change in the NMR spectrum of vacuum distilled dimethyltin diacetate in CDCl₃ on adding D₂O. Failure to observe significant changes at 55°C implies, contrary to previous thinking, an appreciable resistance to "hydrolysis".

Dimethyltin dipropionate, Dimethyltin Diisobutyrate and Dimethyltin Dipivalate.

All of these compounds are new. No previous data has been pub-

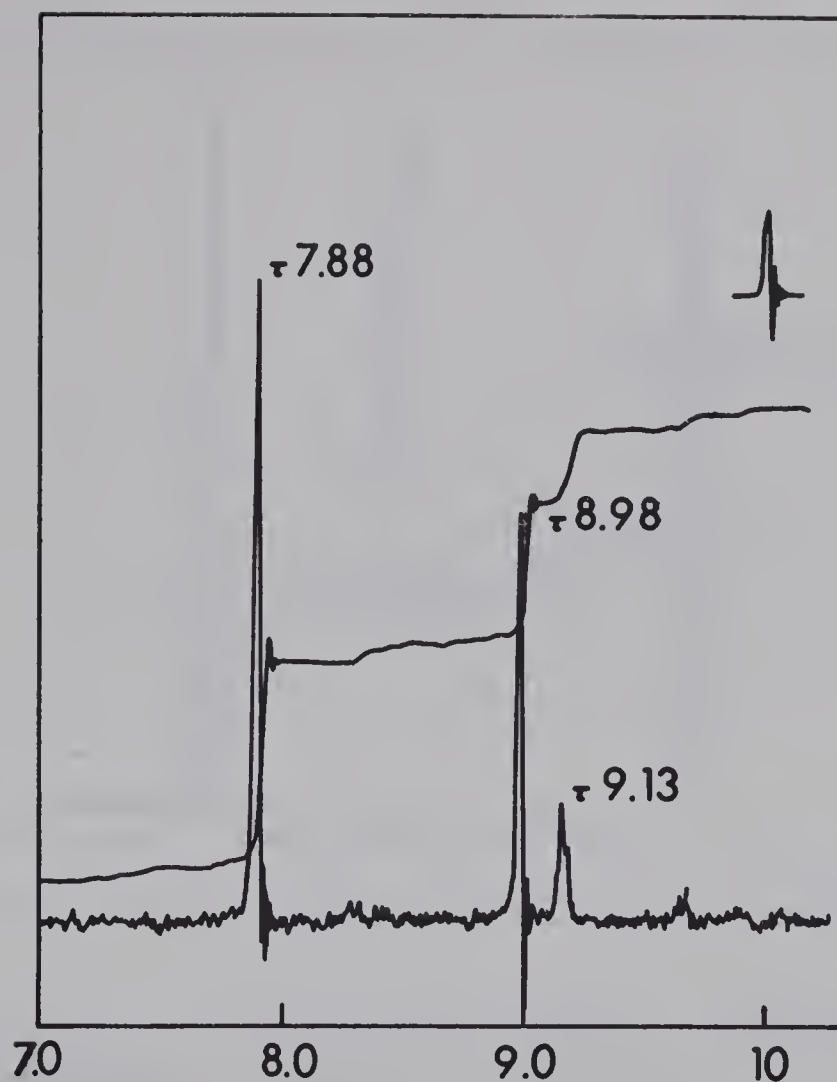


Figure 22a. NMR spectrum of sublimed dimethyltin acetate.

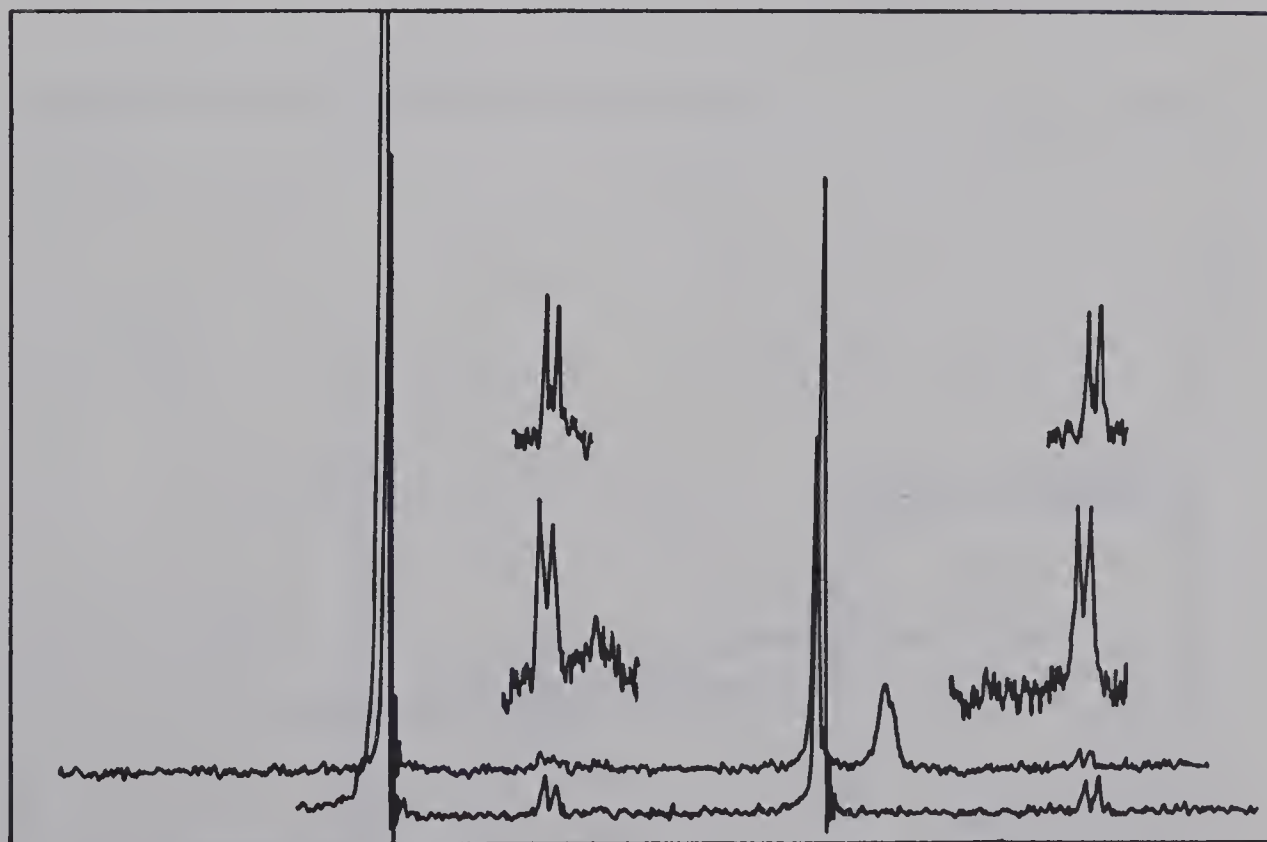


Figure 22b. NMR spectrum of sublimed dimethyltin diacetate before (upper trace) and after (lower trace) adding glacial acetic acid.

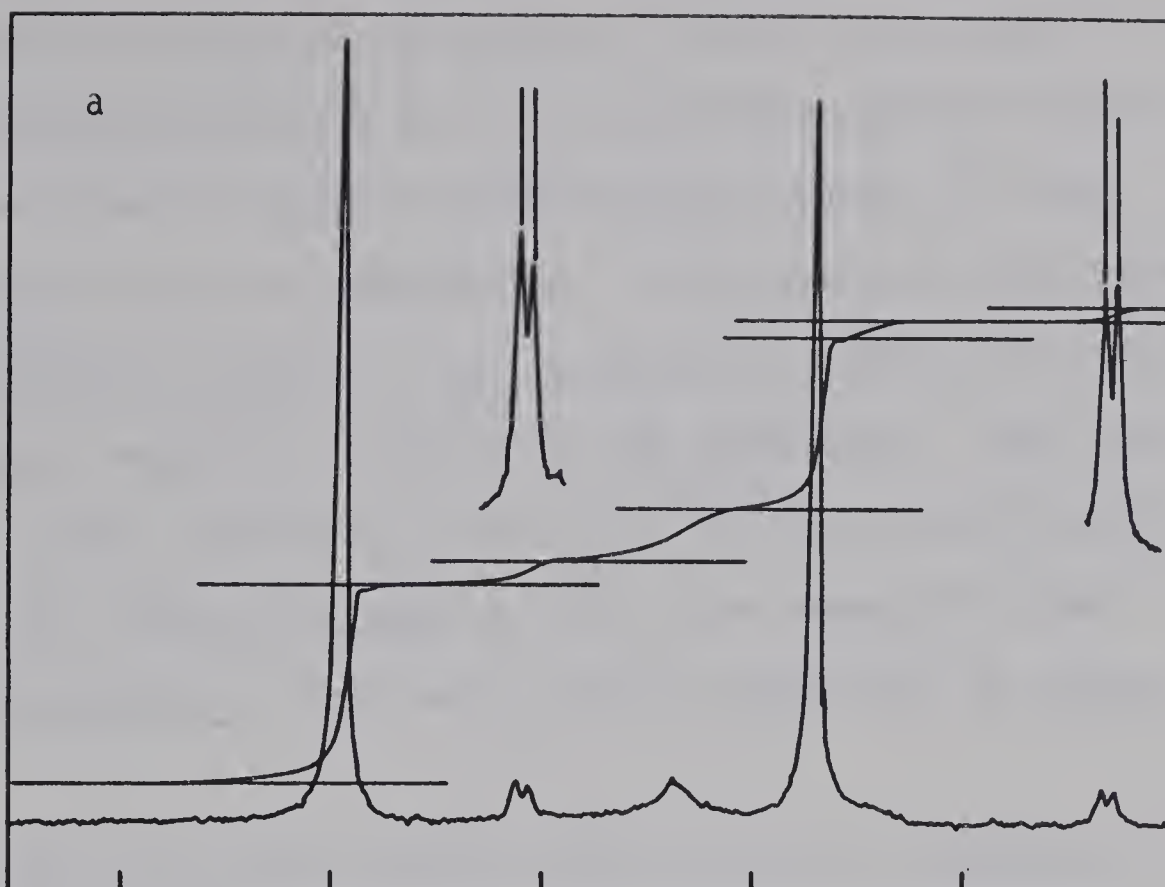
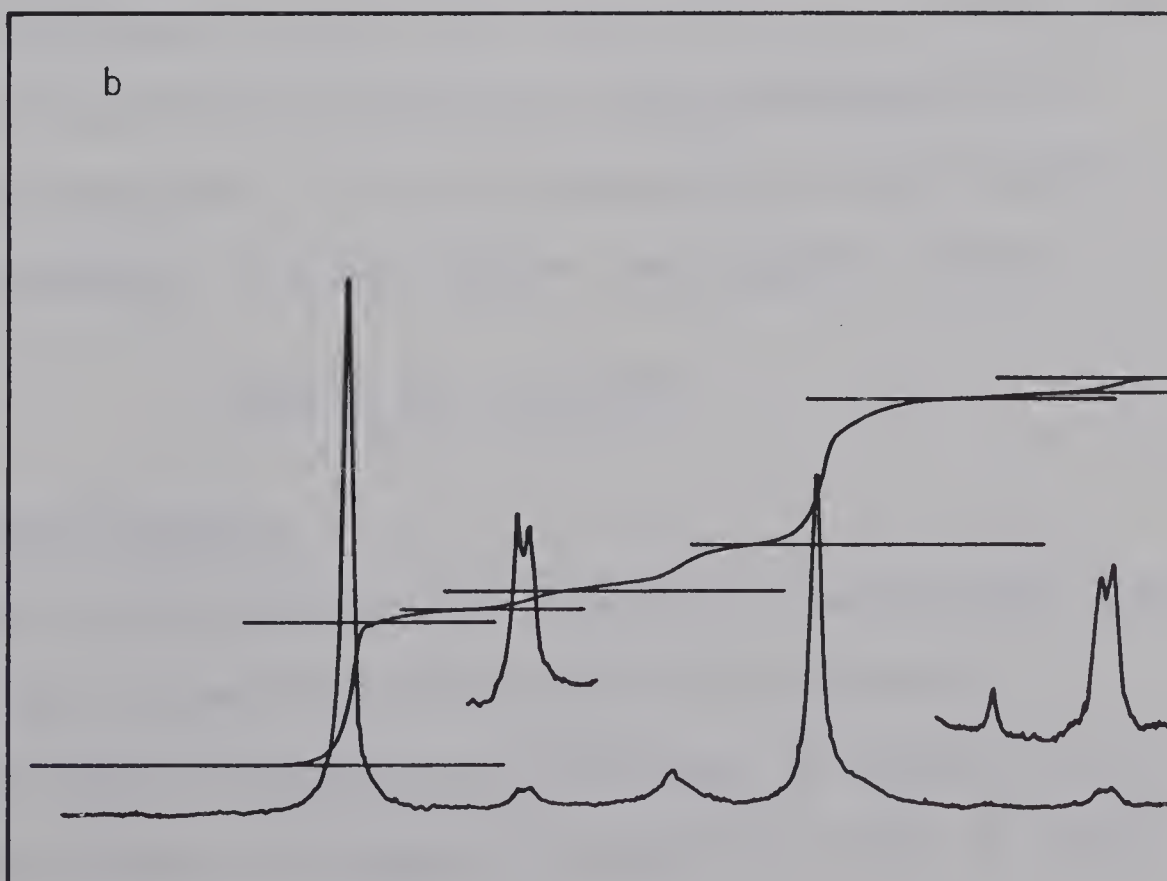


Figure 23. NMR spectra of dimethyltin diacetate: a, before adding D₂O; b, after adding D₂O.



lished; however, it has generally been assumed that they are structurally similar to dimethyltin diformate. Cleavage of the vinyl groups from dimethyldivinyltin with the appropriate carboxylic acid followed by sublimation and/or recrystallization proved to be the most satisfactory method of preparation. It was observed that regardless of the method of synthesis used, trimethyltin carboxylate impurities were always present as indicated by NMR examination. Room temperature high vacuum sublimation proved to be the only suitable method of removing the trimethyltin impurity due to the trimethyltin and dimethyltin carboxylates having very similar solubilities in various solvents.

Satisfactory analytical results were obtained for dimethyltin dipivalate. Dimethyltin diisobutyrate was similar to dimethyltin diacetate in that satisfactory carbon and hydrogen but low oxygen values were obtained. Dimethyltin dipropionate was not isolated in a pure state; however, based on IR and NMR findings there seems little doubt that the material studied was largely the desired compound, contaminated with hydrolysis/condensation product, tetramethyl-1,3-dipropionoxydistannoxane. All of the compounds are sufficiently soluble, as prepared, to allow solution spectroscopic studies.

RESULTS AND DISCUSSION

Molecular Weight Studies.

Dimethyltin dipivalate was the only compound sufficiently pure to permit meaningful molecular weight studies to be conducted.

A small amount of association of some type is indicated in dibromomethane solution. The degree of association (1.08) is surpri-

singly concentration independent. More "normal" behavior is observed in benzene solution. Essentially monomeric behavior is indicated at low concentrations with association (1.19) occurring at higher concentrations.

Infrared Spectra.

Complete infrared data are given in Tables XVI, XVII and XVIII for dimethyltin dipropionate, dimethyltin diisobutyrate and dimethyltin dipivalate respectively. Due to the similarities in spectra the infrared observations are discussed in a more general manner than previously.

Carbonyl-Carboxyl Region.

Two strong absorptions in cyclohexane ($1610-1600\text{ cm}^{-1}$, $1578-1563\text{ cm}^{-1}$) assignable to asymmetric stretching modes appear to indicate a structure very similar to the lower homologue dimethyltin diacetate. In addition absorptions attributable to free carboxylic acid are observed ($1700-1715\text{ cm}^{-1}$). In the solid state spectra, assignment of the $1578-1563\text{ cm}^{-1}$ bands to symmetrically bridged propionate, isobutyrate and pivalate groups is relatively certain as these bands are the strongest observed. Structural differences present in dimethyltin diisobutyrate, or less likely phenomena attributable to the use of Halo oil, may account for the rather high frequency (1605 cm^{-1}) of the stronger absorption observed in this compound.

Tetramethyl-1,3-diisobutyrate distannoxane does not appear to account for the 1605 cm^{-1} band. Separation of the Halo oil mull plates and exposure to laboratory air overnight, a situation which might be expected to increase the concentration of "hydrolysis" pro-

TABLE XVI

INFRARED SPECTRA FOR DIMETHYLTIN DIPROPIONATE.

CHCl ₃ *	Nujol	Propionic Acid C ₆ H ₁₂	C ₆ H ₁₂	CHCl ₃
	1755 <u>sh</u>	1762 vw	1745 <u>sh</u>	1740 w
	1728 <u>w-m</u>	1715 s	1720 <u>w-m</u>	1710 w
1642 <u>sh</u>	1645 m			1662 m
1634 <u>sh</u>				
1628 <u>sh</u>				
1620 <u>sh</u>				
1612 s	1600 m-s		1610 vs	1598 s
	1570 s		1565 w-m	
1553 vs				
1547 vs				
1460 m-s				1458 m
			1392 m-s	1395 m-s
			1385 <u>sh</u>	
			1360 m	1363 m-s
			1308 w-m	1360 m-s
1295 m	1268 s		1268-50 m	1262 m-s
	1247 <u>sh</u>		1202 w	
	1190 <u>w-m</u>		1197 w	
	1186 w-m			
1073 m	1070 m-s		1074 m	1072 m
1005 w-m	1007 m			
			980 vw	
900 <u>sh</u>	896 <u>sh</u>			900 m
885 <u>w-m</u>	892 m-s		890 vw	
	804 m-s		810 m	
	780 m-s		795 m	
	670 m-s		678 w-m, br	
638 m-s				
618 <u>sh</u>				
572 <u>m</u>	575 m			576
	550 m, br			
528 w	528 w-m			528
	522 w-m			
509 m	505 w			

* Solvent treated with anhydrous Al₂O₃ immediately prior to use.

TABLE XVII

INFRARED SPECTRA FOR DIMETHYLTIN DIISOBUTYRATE.

CHCl ₃	C ₆ H ₁₂	Halo-Oil Initial	Plates separated overnight	Isobutyric Acid
		1736 <u>sh</u> 1708 <u>w</u>	1705 vw	1710 s
1687 w, br			1660 <u>sh</u> 1650 <u>sh</u> 1645 <u>sh</u> 1631 m	
1615 <u>sh</u> 1600 <u>s</u>	1610 s	1605 vs 1567 m-s, <u>sh</u> 1470 s	1602 m, <u>sh</u> 1560 vs	
1465 m 1455 w	1558 s		1468 s 1450 w 1420 s 1395 m	1470 w-m 1415 w
1395 m-s	1395 m	1395 vs 1370 <u>sh</u> 1358 <u>s</u>	1355 m-s	
1360 m 1260 m	1360 m			
	1195 w 1165 w			
1095 w 1080 w	1095 w 1080 w 928 w			
905 w 855 w				
	835 w 795 m 645 w-m			
575 w 525 vw				

TABLE XVIII

INFRARED SPECTRA FOR DIMETHYLTIN DIPIVALATE.

CHCl ₃	C ₆ H ₁₂	KBr	Nujol
1739 vw, br	1730 <u>sh</u>	1730 w, br	
1698 vw, br	1700 <u>m</u>	1700 m	1700 vw, br
	1662 m		
		1615 w-m	1617 m
1599 vs	1600 s	1597 w	1588 w-m
1576 vs	1578 m	1568 <u>sh</u>	
1560 <u>sh</u>		1560 <u>sh</u>	1556 <u>sh</u>
	1550 w-m	1555 <u>sh</u>	1550 <u>vs</u>
1544 <u>sh</u>		1548 <u>vs</u>	1545 <u>vs</u>
		1536 <u>sh</u>	1540 <u>sh</u>
		1530 <u>sh</u>	
1479 vs		1480 <u>vs</u>	1480 s
1459 m		1455 w-m	
1423 <u>sh</u>		1420 <u>sh</u>	1418 <u>sh</u>
1400 <u>vs</u>		1410 <u>m-s</u>	1413 <u>s</u>
	1393 m	1400 sh	1392 vw
		1368 m	
1352 vs		1357 m	
	1347 s	1352 <u>sh</u>	
1235 w, br			
	1220 <u>sh</u>	1220 m	1222 s
	1208 <u>s</u>	1204 m, br	1205 w
1030 w		1023 w	1026 vw
	978 vw		
	933 w, br		933 vw
909 m	905 w, br	904 vw	
		890 w	892 w-m
830 w, br	837 <u>sh</u>		
	822 <u>w-m</u>		
	790 m	792 m	793 m
			787 m
		780 <u>sh</u>	778 <u>sh</u>
	745 w-m		
	735 w		
	675 w-m		
		633 m	633 m-s
618 m	618 m		
		602 w	607 <u>sh</u>
575 w-m	572 w-m	577 w-m	573 <u>m</u>
565 <u>sh</u>		558 w	555 w-m
545 w	545 w	547 <u>sh</u>	
525 w		528 <u>sh</u>	524 <u>sh</u>
518 <u>sh</u>		522 w	518 <u>w-m</u>
		498 m	495 m-s

duct, essentially reversed the intensities and nature of the carbonyl absorption, (initially: 1605 cm^{-1} strong and 1567 cm^{-1} shoulder, after exposure: 1602 cm^{-1} shoulder and 1560 cm^{-1} strong).

Assignment of the $1610\text{-}1600\text{ cm}^{-1}$ band to an asymmetric stretching mode of the respective carboxylate group seems certain; however, as mentioned previously, discussion is deferred to the end of this section.

It should be pointed out that absorptions assignable to unassociated carbonyl groups are also observed in the spectrum of dimethyltin dipivalate and dimethyltin dipropionate in cyclohexane solution.

Chloroform solution spectra of each compound contain several interesting features when compared against each other. Dimethyltin diisobutyrate spectra contain only one strong absorption (1600 cm^{-1}) with a shoulder at 1615 cm^{-1} whereas dimethyltin dipivalate spectra show two strong absorptions (1599 and 1576 cm^{-1}) and dimethyltin dipropionate spectra show three, one of which may be viewed as a doublet (1612 , 1553 and 1547 cm^{-1}). It is a strong possibility that the lack of a second strong absorption in the spectrum of dimethyltin diisobutyrate and the presence of two lower frequency absorptions in the dipropionate spectrum are due to concentration effects. A single strong absorption (1598 cm^{-1}) was observed in the spectrum of dimethyltin dipropionate in one instance where the concentration was known to be dilute.

Tin-Carbon Stretching Region.

Each of these compounds appears to possess a non-linear C-Sn-C skeleton in CHCl_3 solution as indicated by absorptions in the regions $580\text{-}570\text{ cm}^{-1}$ and $530\text{-}520\text{ cm}^{-1}$. Solid state studies of dimethyltin

dipivalate in KBr and dimethyltin dipropionate in Nujol reveal the same two absorptions at frequencies essentially identical to those observed in CHCl_3 . Unfortunately, no solid state studies were conducted with dimethyltin diisobutyrate.

NMR Spectra.

NMR parameters of dimethyltin dipropionate, dimethyltin diisobutyrate and dimethyltin dipivalate are listed in Tables XIX, XX and XXI respectively.

Generally these dimethyltin dicarboxylates are characterized by a methyltin resonance in the 9.00-9.20 τ region with spin-spin couplings of appreciable magnitude ($J=80-85$ cps). Variable temperature studies reveal a rather pronounced change in all chemical shifts but little change in the magnitude of J .

Each of these compounds will be discussed independently in view of the large amount of data obtained, the nature of the study and the structural features such data may indicate.

Dimethyltin dipropionate.

Although the analytical results obtained for this compound were poor, the NMR spectrum leaves little doubt as to the identity of the vast majority of the material present. Theoretically, three different types of proton resonances are expected ($\text{CH}_3\text{-Sn}$, singlet; $\text{CH}_3\text{-CH}_2$, triplet; $\text{CH}_3\text{-CH}_2$, quartet) in the ratio 1.5:1.5:1.0, and experimentally three different resonances are observed in the ratio 1.44 singlet; 1.61 triplet; 1.0 quartet. The low $\text{CH}_3\text{-Sn}$ ratio is readily explained due to the presence of tetramethyl-1,3-dipropionoxydistannoxane (vide infra) but the high triplet/quartet ratio is puz-

TABLE XIXa

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTIN DIPROPIONATE.

Solvent	Temp. °C	$\text{CH}_3\text{-}\overline{\text{C}}\text{-Sn}$	J^1 cps	J^2 cps	$\text{CH}_3\text{-}\overline{\text{C}}\text{-CH}_2\text{COO}$	$\text{CH}_3\text{-}\overline{\text{C}}\text{-CH}_2\text{COO}$	
CH_2Br_2	89	9.07			8.96, 8.89 8.81	7.79, 7.72 7.64, 7.57	*
CH_2Br_2	79	9.06	82.9	79.4	8.97, 8.89 8.82	7.79, 7.71 7.64, 7.56	(a)*
CH_2Br_2	46	9.05	83.3	79.8	8.97, 8.89 8.82	7.78, 7.70 7.63, 7.55	*
CH_2Br_2	R.T.	9.05	83.6	80	8.98, 8.90 8.83	7.80, 7.73 7.65, 7.58	(b)*
CH_2Br_2	-20	9.02	84	80.2	8.99, 8.91 8.84	7.77, 7.70 7.62, 7.55	(c)*
CH_2Br_2	-51	9.00	84.9	81.1	8.91 8.84	7.71, 7.64 7.56	(d)*
$\{\text{CH}_2\text{Br}_2$ $\text{C}_5\text{D}_5\text{N}$	+67	9.06	103.7	98.6	8.93, 8.85 8.78	7.77, 7.70 7.62, 7.54	**
$\{\text{CH}_2\text{Br}_2$ $\text{C}_5\text{D}_5\text{N}$	46	9.05	106.3	101.6	8.92, 8.84 8.77	7.75, 7.67 7.60, 7.52	(e)
$\{\text{CH}_2\text{Br}_2$ $\text{C}_5\text{D}_5\text{N}$	0	9.02	109.8	105	8.89, 8.81 8.74	7.69, 7.62 7.55, 7.47	(f)
$\{\text{CH}_2\text{Br}_2$ $\text{C}_5\text{D}_5\text{N}$	-20	9.03	111.2	106.2	8.91, 8.83 8.76	7.68, 7.60 7.53, 7.45	
$\{\text{CH}_2\text{Br}_2$ $\text{C}_5\text{D}_5\text{N}$	-41	9.05	111.7	106.9	8.93, 8.85 8.78	7.70, 7.63 7.56, 7.48	

* 105 mg/0.3 ml, Internal TMS.

** 105 mg/ 0.3 ml CH_2Br_2 , 0.5 ml $\text{C}_5\text{D}_5\text{N}$, Internal TMS.

(a) Impurity 9.24 τ very broad.

(b) Impurities 9.24 and 9.26 τ .

(c) Impurities 9.24 τ , $J=91$ cps; 9.26 τ , $J=85$ cps.

(d) Impurities 9.24 and 9.25 τ ; $J \approx 86.5$ cps; $\text{CH}_3\text{-}\overline{\text{C}}\text{-CH}_2$, signal very broad.

(e) Impurities 9.08 and 9.13 τ .

(f) Impurity 9.09 τ .

TABLE XIXb

Solvent	Temp. °C	$\text{CH}_3\text{-}\overline{\text{C}}\text{-Sn}$	J^1 cps	J^2 cps	$\text{CH}_3\text{-}\overline{\text{C}}\text{-CH}_2\text{COO}$	$\text{CH}_3\text{-}\overline{\text{C}}\text{-CH}_2\text{COO}$	
CHCl_3	R.T.	9.15	82.4	78.8	9.04, 8.96 8.89	7.85, 7.78 7.71, 7.64	(g)
Ratio Theory		1.44 1.50			1.61 1.50	1 1	
CHCl_3	50	9.15	82.6	79.2	9.04, 8.97 8.90	7.87, 7.80 7.73, 7.66	(h)
CHCl_3	30	9.17	82.4	78.8	9.06, 8.99 8.92	7.87, 7.80 7.73, 7.66	(i)
CHCl_3	-30	9.17	83.1	79.2	9.11, 9.04 8.96	7.88, 7.81 7.74, 7.67	(j)
CHCl_3	-50	9.18	83.3	79.4	9.13, 9.06 8.98	7.89, 7.82 7.75, 7.68	
CHCl_3 $\text{C}_5\text{D}_5\text{N}$	+55	9.67	101.8	97.5	9.50, 9.43 9.36	8.35, 8.28 8.21, 8.14	(k)***
CHCl_3 $\text{C}_5\text{D}_5\text{N}$	30	9.79	106.2	103.8	9.62, 9.55 9.48	8.46, 8.39 8.32, 8.25	(l)***
CHCl_3 $\text{C}_5\text{D}_5\text{N}$	0	9.92	108.7	104	9.75, 9.67 9.60	8.57, 8.50 8.43, 8.36	***
CHCl_3 $\text{C}_5\text{D}_5\text{N}$	-30	10.05	110.2	105.3	9.89, 9.81 9.74	8.70, 8.62 8.55, 8.48	***
CHCl_3 $\text{C}_5\text{D}_5\text{N}$	-50	10.16	≈ 111		10.00, 9.93 9.85	8.00, 8.73 8.65, 8.58	***

*** 218 mg/0.3 ml Al_2O_3 dried CHCl_3 +0.5 ml $\text{C}_5\text{D}_5\text{N}$, benzene reference.

(g) Impurities 9.31 and 9.33 τ ; concentration 218 mg/0.3 ml Al_2O_3 dried CHCl_3 benzene reference.

(h) Impurities 9.33 and 9.35 τ .

(i) Impurities 9.34 and 9.36 τ .

(j) Impurities 9.39 and 9.41 τ .

(k) Impurities 9.74 and 9.80 τ .

(l) Impurities 9.87 and 9.93 τ .

TABLE XX

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTIN DIISOBUTYRATE (a).

Solvent	Temp. °C	Conc. mg/ml	CH ₃ -Sn τ	J ¹ cps	J ² cps	H-C(CH ₃) ₂ τ	H-C(CH ₃) ₂ τ
CDCl ₃	50	560	9.09	84	80.3	7.43	8.88, 8.77
CDCl ₃	41	560	9.07	84.4	81	7.35	8.86, 8.74
CDCl ₃	0	560	9.02	85	81	7.30	8.82, 8.71 (b)
CDCl ₃	-30	560	9.01	85.6	81.8	7.30	8.82, 8.71
CDCl ₃	-50	560	8.98	86.8	82.7	7.25	8.80, 8.68
CDCl ₃	+41	560	9.06	84.2	80.6	7.43 major 7.40 minor	8.86, 8.74 (c)
{CDCl ₃ C ₅ D ₅ N	55		9.12	103.2	98.5	7.43	8.87, 8.76 (d)
{CDCl ₃ C ₅ D ₅ N	41		9.10	107.3	102.3	7.38	8.83, 8.72 (d)
{CDCl ₃ C ₅ D ₅ N	0		9.08	111.5	106.5	7.38	8.80, 8.68 (d)
{CDCl ₃ C ₅ D ₅ N	-30		9.05	112	107	7.30	8.76, 8.72 (d)
CDCl ₃	41		9.18 9.06				8.87, 8.75 (e)

(a) Internal TMS, A-60 and A56-60A spectrometer.

(b) Impurities 9.18 and 9.22 τ .

(c) After variable temperature study.

(d) 0.3 ml CDCl₃ + 0.3 ml C₅D₅N; Internal TMS.

(e) CDCl₃ layer of hydrolysis product.

TABLE XXI

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTIN DIPIVALATE.

Solvent	Conc. mg/ml	Temp. °C	CH ₃ -Sn τ	J ¹ cps	J ² cps	(CH ₃) ₃ C-COO τ
CDCl ₃ (a)	553	33.5	9.05	84.6	80.7	8.72
CDCl ₃ (a)	507	33.5	9.04	83.6	79.9	8.71
CDCl ₃	660	55	9.16	83.0	79.3	8.82
CDCl ₃	660	33.5	9.15	83.2	79.5	8.82
CDCl ₃	660	0	9.16	83.4	79.6	8.84
CDCl ₃	660	-20	9.15	83.5	79.8	8.84
CDCl ₃	660	-40	9.15	83.7	79.9	8.84
{ CDCl ₃ (b) C ₅ D ₅ N		55	9.12	107.9	103.4	8.75
{ CDCl ₃ (b) C ₅ D ₅ N		33.5	9.12	108.2	103.2	8.75
{ CDCl ₃ (b) C ₅ D ₅ N		0	9.13	110.5	105.3	8.74
{ CDCl ₃ (b) C ₅ D ₅ N		-20	9.13	110.8	105.8	8.74

100 mHz; Benzene reference unless noted otherwise.

(a) 60 mHz; External TMS.

(b) 0.3 ml CDCl₃ + 0.5 ml C₅D₅N.

zling and the reasons for its occurrence remain unknown.

Complete studies were conducted in CH_2Br_2 at approximately 330 mg/ml and in CHCl_3 at approximately 720 mg/ml. NMR parameters observed in each solvent are given in Tables XIXa and XIX b. Inspection of the tables reveals several interesting but puzzling features. The chemical shifts observed in CHCl_3 at a relatively high concentration are appreciably different from those observed in CH_2Br_2 at about half the concentration, yet the spin-spin coupling constants are almost identical. At first glance it would seem logical to attribute the differences in chemical shifts to the different reference standards used with each solvent. This possibility was rejected after determination of the chemical shift of CH_2Cl_2 in CHCl_3 relative to internal TMS and internal benzene. Essentially the same chemical shift value was obtained with either reference. It is also possible that the presence of even a small amount of benzene may have unusual effects due to some unknown phenomenon associated with benzene-methyltin interactions. Changes in spectra in the presence of benzene have been noted in other systems (56); however, the explanation must be considered a matter of speculation.

Two less intense resonances attributed to the impurity (9.31 and 9.33 τ / CHCl_3 ; 9.24 and 9.26 τ / CH_2Br_2) are assigned to methyl groups on tin in view of spin-spin couplings being associated with each resonance (9.24 τ , $J \approx 89$ cps; 9.26 τ , $J \approx 88$ cps). Couplings are undoubtedly associated with the 9.31 and 9.33 τ resonances also but are not observed at the concentration studied where the intensity of even the parent resonance signal was weak.

Variable temperature studies of the CHCl_3 solution (+50°— -50°C)

and CH_2Br_2 solution ($+89^\circ$ — -51°C) indicate small changes in the chemical shifts and the magnitude of J . Apparently some type of exchange phenomenon occurs either within each compound or between compounds as the spin-spin couplings associated with the CH_3 -Sn resonance (9.07τ) are unresolvable at 89°C . Additionally the two less intense impurity resonances (9.24 and 9.26τ) have coalesced to a single, broad peak (9.24τ) at 79°C and appear as a very broad and rather flat hump at 89°C . Interactions of this type have recently been observed in other methyltin systems (57, 58).

Complex Formation Studies.

Adding pyridine- d_5 to the CHCl_3 or CH_2Br_2 solution brings about the expected increase in the magnitude of J and upfield shift in the observed resonances. Complete data are given in Tables XIXa and XIXb.

The magnitude of J near room temperature ($106.2\text{ cps}/30^\circ\text{C}$; CHCl_3) is slightly larger than that observed in other complexed dimethyltin species [$\text{Me}_2\text{SnCl}_2 \cdot (\text{H}_2\text{O})_x$, 101.9 cps ; $\text{Me}_2\text{Sn}(\text{acac})_2$, 99.3 cps ; $\text{Me}_2\text{Sn}(\text{hfacac})_2^*$, 103.4 cps] suggestive of a similar structure. Pronounced changes occur in both the magnitude of J and the location of the resonances when the temperature is varied. The magnitude of J at -50°C (111 cps) is similar to values recently reported by Kitching for dimethyltin compounds in strongly complexing solvents (113 cps) (58), the highest values of J reported for dimethyltin species thus far.

Some type of equilibrium seems indicated as several correlations are possible. Figure 24 illustrates the linear relationship observed between the chemical shift of the CH_3 -Sn group and temperature. Similarly the methyltin resonance plotted against the propionate methyl

* (hfacac) = hexafluoro acetylacetonate.

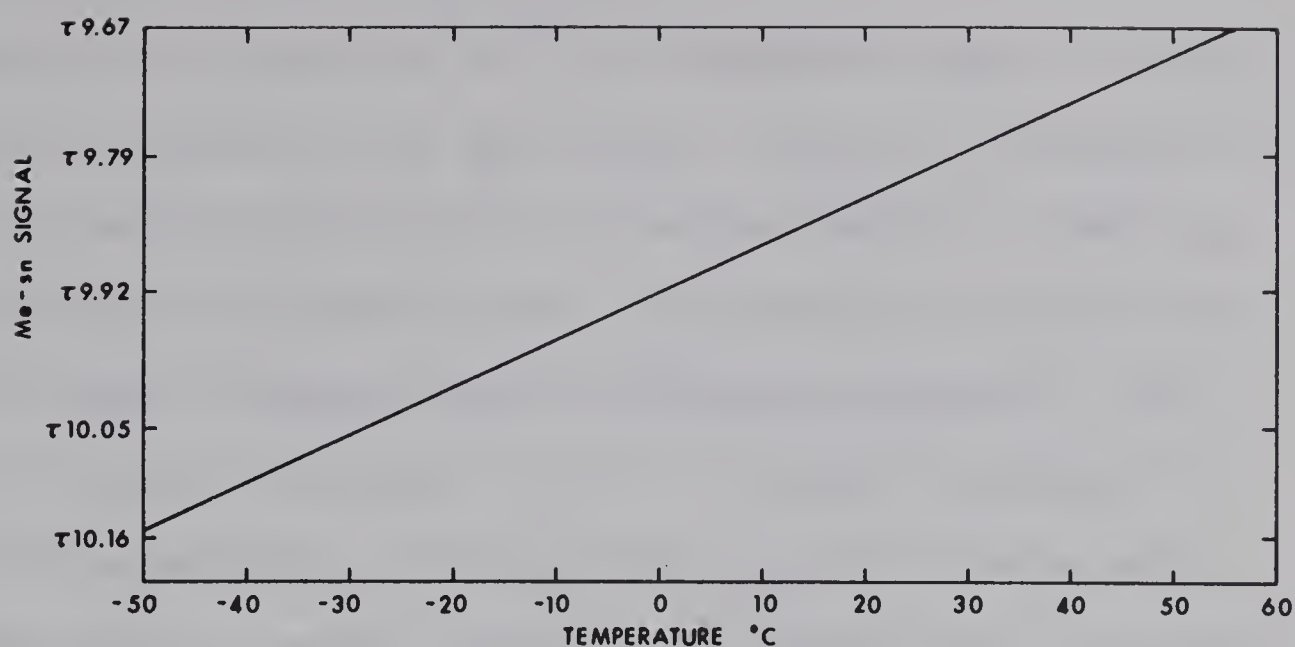


Figure 24. Methyltin chemical shift and temperature relationship for dimethyltin dipropionate.

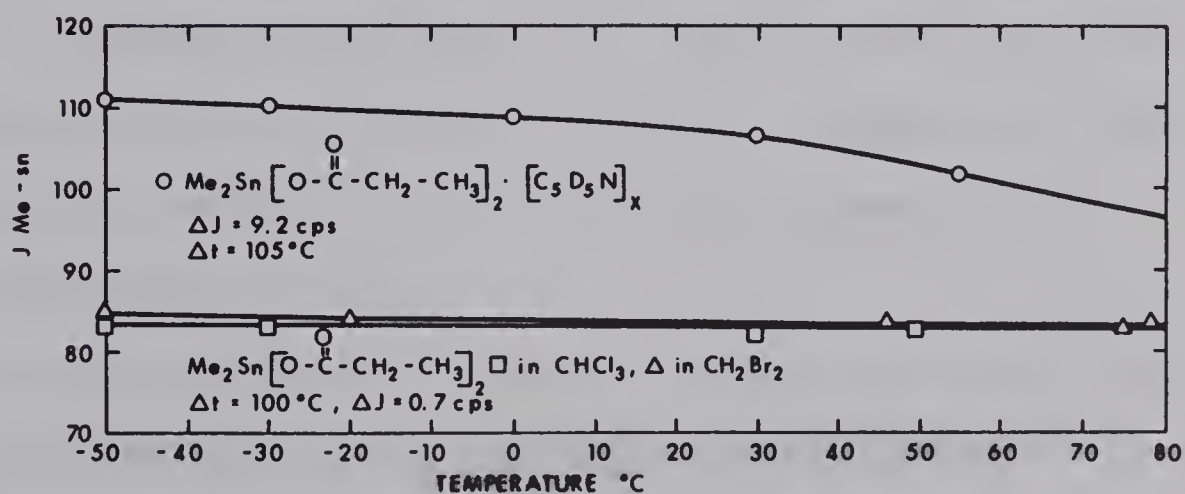


Figure 25. Change in methyltin coupling (J) with temperature for complexed and uncomplexed dimethyltin dipropionate.

resonance signal yields a straight line.

Changes in the magnitude of J with temperature appear to present the clearest indication of an equilibrium. Figure 25 illustrates the curves obtained with complexed and uncomplexed material. Some type of change occurs near 20-30°C in the complexed material while essentially no change is observed with the uncomplexed material. Additionally, as might be expected, a plot of the $\text{CH}_3\text{-Sn}$ resonance vs J results in a smooth curve. The equilibrium may well involve monomeric and associate species; however it is suggested that the changes in geometry of the dimethyltin portion are relatively small.

Dimethyltindiisobutyrate.

Table XX lists the NMR parameters. Methyltin resonance is observed at 9.07 τ with symmetrically disposed spin-spin couplings $J=84.4$ cps. A doublet assignable to the methyl groups of the isobutyrate is observed at 8.86 and 8.74 τ , and a quintet due to the single isobutyrate proton is centered at 7.35 τ . Integration of the signal intensities revealed a ratio in excellent agreement with theory $[\text{CH}_3\text{-Sn}/\text{H-C}(\text{CH}_3)_2 = 0.5]$.

Changes in the magnitude of J and the chemical shifts with temperature are very similar to those observed with dimethyltindi propionate. Methyltin resonances believed due to tetramethyl-1,3-diisobutyrate distannoxane are observed at 9.18 and 9.22 τ at 0°C. No permanent change occurs on varying the temperature as re-examination of the sample at room temperature following variable temperature studies gave values essentially identical to those obtained before varying the temperature.

Complex Formation Studies.

Pyridine- d_5 addition brings about the expected changes in the spectrum, the magnitude of J near room temperature (107.3 cps/41°C) is again larger than that of other complexed dimethyltin species. Increasing the temperature results in a decreased J value (103.2 cps) and upfield shift in all resonances. Decreasing the temperature has the opposite effect with J (112 cps/-30°C) approaching the assumed limiting value 113 cps, and the chemical shifts appearing at lower field strengths.

Examination of the organic layer following addition of D_2O to dimethyltindiisobutyrate revealed two resonances assignable to methyl groups on tin (9.06 and 9.18 τ) and two resonances due to the methyl groups of the isobutyrate molecule (8.75 and 8.87 τ).

Dimethyltindipivalate.

Dimethyltindipivalate exhibits a single sharp resonance at 9.04 τ relative to a TMS external standard with $\underline{CH_3}$ -Sn couplings $J \approx 84$ cps (Table XXI). The pivalate resonance is observed at 8.71 τ . Small changes in J and the chemical shifts are observed with varying concentration.

A marked change in chemical shifts occurs when benzene is used as an internal standard. Changes in spectra in the presence of benzene have been noted previously. Single, sharp resonances are observed at 9.15 τ with couplings $J=83.2$ cps and 8.82 τ due to methyltin and pivalate protons respectively.

Chemical shifts and J are essentially unchanged over a 95°C temperature range. The magnitude of J is roughly comparable to that reported (58) for the bis DMSO adduct of dimethyltindichloride in

chloroform ($J=86$ cps) and dimethyltin diacetate (35) in carbon tetrachloride ($J=82.5$ cps), both of which show little change in J with temperature.

Complex Formation Studies.

The chemical shift of the pivalate and methyltin resonances increase to 8.75τ and 9.12τ respectively and J increases to 108 cps on adding a large excess of pyridine- d_5 to the chloroform solution. Temperature variation over a 75°C range produces a noticeable change in J (108 cps/ 55°C ; 111 cps/ -20°C). The magnitude of J is nearly equal to that observed for other dimethyltin compounds in the presence of complexing agents as illustrated in Table XXII.

Infrared and NMR Structural Implications.

Indications of non-linear C-Sn-C geometry appear to rule out the presence of a regular trans octahedral monomeric or bridged dimethyltin species and a normal trans trigonalbipyramidal configuration. Additionally, the trigonal bipyramidal structure appears most unlikely as such a structure would require an equal proportion of unassociated ester-like and associated carboxylate groups, and the infrared spectra clearly indicate such is not the case. The most pronounced $-\text{CO}_2-$ absorption observed ($1600\text{--}1630\text{ cm}^{-1}$) is intermediate between that of an unassociated, ester-like group ($\approx 1650\text{ cm}^{-1}$) and a presumably symmetrically bridged $-\text{CO}_2-$ group ($\approx 1580\text{ cm}^{-1}$). It is entirely reasonable to presume that the vibrational mode giving rise to this intermediate $-\text{CO}_2-$ absorption is essentially the same in all systems where it is observed.

The following proposed structure is believed to be consistent

TABLE XXII

EFFECT OF EXCESS DONOR LIGAND ON SPIN-SPIN COUPLING PARAMETER J

Compound	Solvent	J cps	Ref.
Me_2SnCl_2	CDCl_3	71	(32)
Me_2SnCl_2	D_2O	107.5	(59)
Me_2SnCl_2	DMSO	113	(58)
$\text{Me}_2\text{SnCl}_2 \cdot \text{D}_2$	H_2O	107	(58)
$\text{Me}_2\text{SnA}_4\text{B}_2$	CH_2Cl_2	56	(56)
$\text{Me}_2\text{SnA}_4\text{B}_2$	DMF	110-113	(56)
$\text{Me}_2\text{SnD}_4\text{B}_2$	CH_2Cl_2	65, 57	(56)
$\text{Me}_2\text{SnD}_4\text{B}_2$	DMSO	110-113	(58)
$\text{Me}_2\text{SnC}_4\text{B}_2$	CH_2Cl_2	57	(56)
$\text{Me}_2\text{SnC}_4\text{B}_2$	DMA	110-113	(56)

A = Dimethylformamide = DMF.

B = Tetraphenylboron.

C = Dimethylacetamide = DMA.

D = Dimethylsulfoxide = DMSO.

with all of the experimental data obtained and to be more reasonable than previously proposed structures.

The frequency of the $\text{-CO}_2\text{-}$ vibration is believed to indicate the carbonyl group of the carboxylate moiety is either donating a small portion of its electron density to a tin atom, or the electron density is more polarized than in an ester-like configuration. The association to tin may be either intra- or intermolecular. Both possibilities will be considered and the preferred structure indicated.

Assuming the average species under study is monomeric, the molecule is viewed as a distorted cis octahedron with the carbonyl oxygen atom of the carboxylate groups "long bonded" to the metal atom. The metal atom thus has six nearest neighbors; however, only four of these neighbors are bonded by covalent type bonds. Why these compounds should contain both long-bonded and bridging $\text{-CO}_2\text{-}$ groups is believed to be a consequence of the geometry of the Sn-C_2 portion of the molecule. It is possible that the approach of the carbonyl oxygen atom of the carboxylate group forces the methyl groups on tin away from the assumed tetrahedral angle initially present. However, a combination of methyl-tin/carboxylate oxygen steric interactions and an insufficient positive effective nuclear charge on tin do not favor a complete conversion from tetrahedral to trans linear geometry. A certain amount of fully bridged material is present; however, the relatively low intensity of this absorption appears to indicate that when possible the molecule will adopt another configuration. The bridged species may be chelated, but rather precise molecular weight studies would be necessary to clarify this point.

Intermolecular association could also account for the observed

-CO₂- absorptions following the same arguments put forth for the monomeric intramolecularly associated species. Such a structure would be analogous to that proposed for the trimethyltin carboxylates discussed in Chapter II. Additionally, this structure may be viewed as a precursor to the fully bridged species observed. It is quite similar to the structures assumed to exist in polymeric trimethyltin carboxylates (25, 26, 27). Intermolecular association is consistent with the observed molecular weight data, whereas chelation would not cause an increased molecular weight. It must be emphasized that extensive molecular weight studies must be conducted before this matter may be decided definitely.

The non-linearity of the Sn-C₂ skeleton is confirmed by the observed NMR spin-spin coupling constants. The magnitude of J apparently indicates the presence of predominantly six-coordinate tin. The hypothesis that the magnitude of J is indicative of the coordination state of the tin atom and thus the distribution of s-character among the bonding orbitals has very recently been questioned by Kitching (53). Based on IR and UV data, he concluded that Me₂SnCl(OX)* and Me₂Sn(OX)₂ contain chelated oxinate groups with 5- and 6-coordinate tin, respectively. If the coordination state is of considerable importance, and if all of the bonds to tin are largely covalent, then the hybridization of the tin orbitals must be different in the two cases, with a corresponding different distribution of s-character among the 5 or 6 orbitals employed in each molecule. Alternatively, if three center pσ bonding is invoked, a similar difference in s-character distribution is implied. Examination of

* = 8-hydroxy quinolate = oxinate.

MeSnCl_2 , $\text{Me}_2\text{SnCl}(\text{OX})$ and $\text{Me}_2\text{Sn}(\text{OX})_2$, containing 4-, 5- and 6-coordinate tin, respectively, indicated "there is no systematic variation in J , although there appears little question that the hybridization of the tin bonding orbitals must be different in the three cases." The values of J for the three compounds in CHCl_3 are 70, 77 and 71 cps respectively (53).

Grant and Litchman (60) have cautioned that in addition to "s" character in a bond, factors such as effective nuclear charge may be important in spin-spin couplings. McFarlane (61) has questioned the assumption of Holmes and Kaesz (32) that $J(^{119}\text{Sn}-\text{CH}_3) = 0$ for a pure $p\pi$ orbital, as a correlation of $J(^{119}\text{Sn}-^{13}\text{C})$ and $J(^{119}\text{Sn}-\text{C}^1\text{H}_3)$ does not pass through the origin.

Schlemper (62) on the other hand has suggested that the magnitude of J may be an indication of the C-Sn-C angle and as such lends support to the suggested relationship between J and tin orbital hybridization.

Dimethyltin diacetate has been suggested to have a distorted octahedral configuration with six-coordinate tin and a presumably non-linear Sn-C₂ configuration, regarded as being distorted from trans (35).

The data presented here are believed to suggest that dimethyltin dicarboxylates in general exist in solution, and presumably also in the solid state, as octahedral-type molecules with the methyl groups predominantly cis or distorted from cis. Alternately, the structure may be viewed as a distorted tetrahedron with four covalent type bonds and two long-bonded oxygen donor atoms.

A crystallographic study (62) of dimethyltin-bis-(8-hydroxy-

quinolinate) has recently shown that it exists as a distorted octahedron with the methyl groups distorted from a cis configuration (C-Sn-C angle $110.7 \pm 0.8^\circ$). The majority of previous spectroscopic investigations on this compound (20, 53, 63, 64, 65) had suggested a predominantly trans arrangement for the methyl groups. In the cis form, the methyl groups would be equivalent by NMR and both the symmetric and asymmetric tin-carbon stretching modes would be infrared active. The presence of the trans isomer in solution cannot be ruled out; however, unless it were distorted, the symmetric Sn-C stretching mode would be infrared inactive. In the dicarboxylates reported here, experimental observations may be accommodated by the suggestion that the carboxylate groups are either "long bonded" chelated or possibly bidentate "long bonded" or symmetrically bonded between two molecules. The latter suggestion is consistent with the observation of association in methylene bromide, and the concentration dependent higher value in benzene observed with dimethyltin dipivalate.

In view of Schlemper's findings regarding the C-Sn-C bond angle in six-coordinate $\text{Me}_2\text{Sn}(\text{OX})_2$, the following gross over-simplification has been used to suggest the C-Sn-C bond angle in the dimethyltin dicarboxylates studied.

- The line in Figure 26 is drawn with the following assumptions,
1. The effective nuclear charge is essentially equal in all cases.
 2. The coordination state of the tin atom is not of major importance.
 3. The electronegativities of the ligands are not significantly different from each other.
 4. Me_2SnCl_2 and $\text{Me}_2\text{Sn}(\text{acac})_2$ exist as tetrahedral and trans-octahedral molecules respectively.

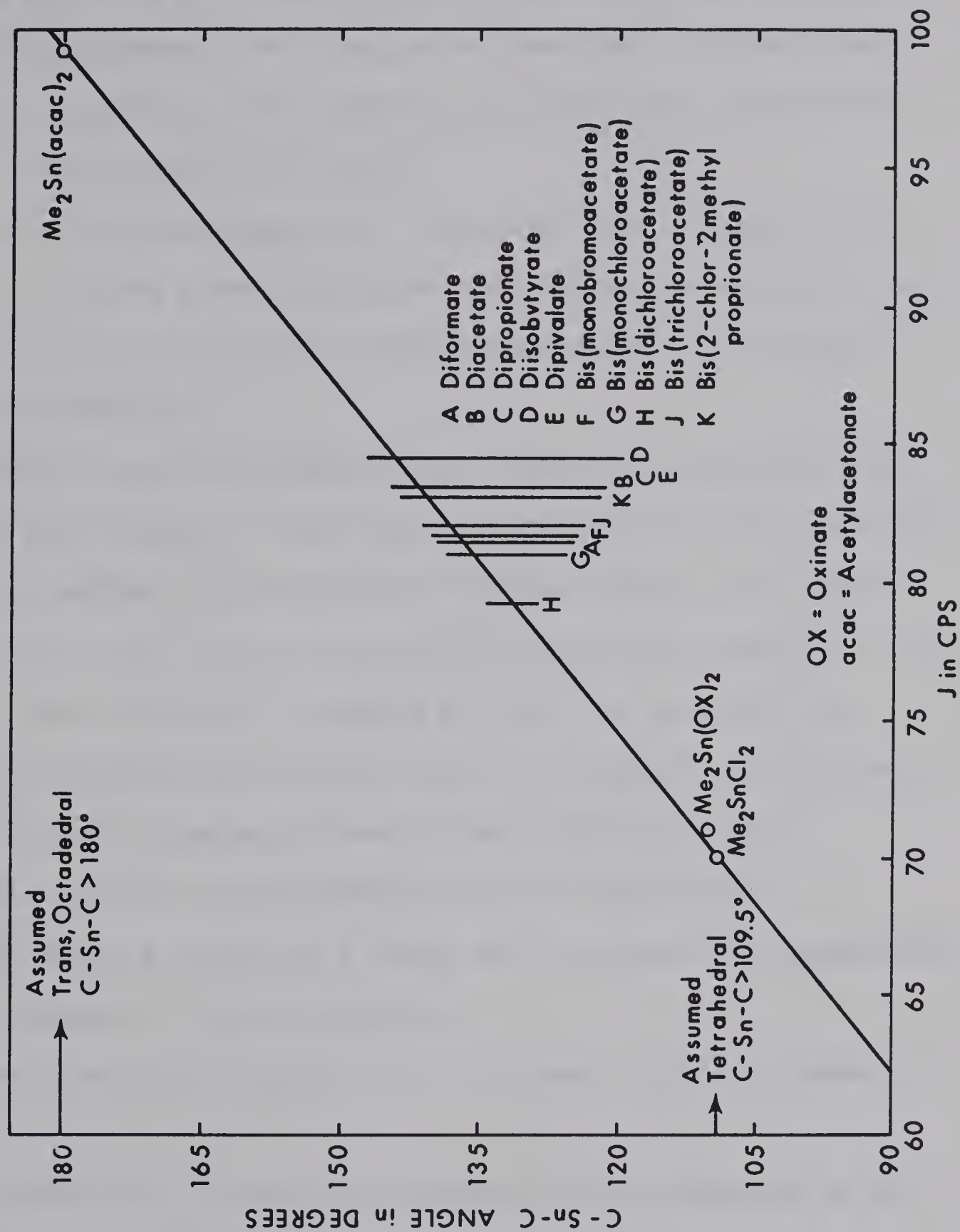


Figure 26. Postulated relationship between C-Sn-C bond angle and methyltin coupling (J).

5. The magnitude of J changes linearly with the C-Sn-C bond angle.

It may be merely fortuitous coincidence that the "predicted" angle for $\text{Me}_2\text{Sn}(\text{OX})_2$ (112°) agrees so well with that determined by x-ray crystallography ($110.7 \pm 0.8^\circ$).

The bond angles suggested in Table XXIII are derived from the figure. They are given in the hope that they may be helpful in x-ray investigations of dimethyltin compounds which will be necessary to test the hypothesis.

Complex formation produces rather remarkable changes, and most workers have assumed in such cases that the species being studied in solution involved a six-coordinate tin atom; however, the dramatic increase in J (27 cps) on dissolving six-coordinate compounds in the donor ligand (Table XXII) suggests at least four possibilities.

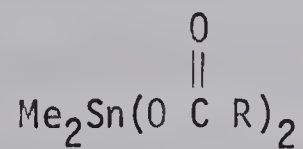
1. The compound becomes largely ionic, i.e. $\text{Me}_2\text{Sn}^{++}$, with predominantly ion-dipole bonding of donor ligands (20, 66, 67, 62).
2. The effective nuclear charge is altered significantly.
3. The geometry changes to a linear Sn-C₂ skeleton with accompanying rehybridization of the tin orbitals.
4. The coordination state of tin is increased from six to seven or more.

Unfortunately, conductivity studies were not conducted so the first possibility remains.

The importance of effective nuclear charge is apparently demonstrated by the comparison of three molecules reportedly containing linear Sn-C₂ skeletons. The coupling constant increases with increasing effective positive charge on tin: $\text{Me}_2\text{Sn}(\text{OH})_4$ $\bar{J}=83$ cps; $\text{Me}_2\text{Sn}(\text{acac})_2$ $J=100$ cps, $\text{Me}_2\text{Sn}^{++}$ $J=108$ cps.

TABLE XXIII

PREDICTED C-Sn-C BOND ANGLES FOR DIMETHYLTIN DICARBOXYLATES.



R	C-Sn-C bond angle in degrees	R	C-Sn-C bond angle in degrees
H	136	CH ₂ Br	137
CH ₃	142	CH ₂ Cl	136
CH ₂ CH ₃	142	CHCl ₂	131
CH(CH ₃) ₂	144	CCl ₃	138
C(CH ₃) ₃	142	C(CH ₃) ₂ Cl	140

The remaining aspect, i.e. coordination state of the metal atom, is meaningful only if the molecules in the inner coordination sphere have a degree of covalent character in their bonding to the metal atom. The solvation of the highly charged dimethyltin cation could easily raise the actual coordination state of the metal atom to seven or conceivably eight. Separation of these potential effects will require further study.

It must be noted that the structures of the complexed dimethyltin dicarboxylates await X-ray crystallographic study; however, based on chemical intuition it is suggested that in the pyridine and DMSO adducts the large value of J observed may be explained as arising from a combination of a seven-coordinate species with both carboxylate groups chelated, one donor pyridine molecule and the methyl groups trans, in rapid equilibrium with a poorly solvated dimethyltin cation.

DIMETHYLTIN BIS (HALO CARBOXYLATES)

Dimethyltin bis(monochloroacetate), dimethyltin bis(dichloroacetate), dimethyltin bis(trichloroacetate) and dimethyltin bis(monobromoacetate) have all been prepared previously (68) but no structural studies have been reported. Dimethyltin bis(α -chloroisobutyrate) or more correctly dimethyltin bis(2-chloro-2-methyl propionate) is a new compound and as such has also not been studied.

All five compounds were prepared by cleavage of vinyl groups from dimethyldivinyl tin with the appropriate carboxylic acid. Small amounts of the corresponding trimethyltin carboxylate were detected in all preparations. Recrystallization removed some of the trimethyltin impurity but failed to yield a pure product. Again, room temperature sublimation proved to be the only satisfactory method of completely removing the impurity. Interestingly enough, continued sublimation resulted in isolation of the compound in a pure state. Decomposition during sublimation does not appear to be an important factor.

Due to structural similarities the halo-substituted acetic acid dicarboxylates will be discussed together and the chloroisobutyrate compound separately.

All halo-substituted carboxylate compounds are readily soluble, as prepared, in spectroscopic solvents.

RESULTS AND DISCUSSION

Most authors have assumed that the dimethyltin bis(halocarboxylate) compounds are analogous to either the higher members of the series, i.e. monomeric, chelated dibutyltin dicarboxylates, or the one dimethyltindicarboxylate studied, i.e. polymeric dimethyltindi-formate.

Experimental results presented here should remove the analogies and assumption heretofore necessary in discussing these compounds.

Molecular Weight Studies.

Anomalous results were obtained in dibromomethane. Dimethyltinbis(monobromoacetate), dimethyltinbis(monochloroacetate) and dimethyltinbis(dichloroacetate) all show a small degree of association at low or moderate concentrations (Table XXIV). Surprisingly the behavior at low and high concentrations is exactly opposite to that normally expected for dimethyltin bis(monochloroacetate). If the molecular weight data is accepted as accurate then the observation of a decrease in molecular weight at relatively high concentration is unusual. The widely varying experimental values obtained for dimethyltinbis(dichloroacetate) imply that unknown factors may be operative in molecular weight determinations in solution.

Dimethyltinbis(2-chloro-2-methyl propionate) shows a degree of association (Table XXIV) in dibromomethane slightly larger than the chloroacetates and somewhat smaller than the bromoacetate analogue. Surprisingly, the molecular weight in benzene (455: d.a. 1.16) is lower than that in the more polar dibromomethane, at nearly equivalent concentrations. The reverse phenomenon would have been expected if the associated species were readily broken up by polar solvents, as was found with trimethyltin formate.

Infrared Spectra.

Complete infrared data for dimethyltinbis(monochloroacetate), dimethyltinbis(dichloroacetate), dimethyltinbis(trichloroacetate) and dimethyltinbis(monobromoacetate) are given in Tables XXV, XXVI, XXVII

TABLE XXIV

DIMETHYLTIN BIS (HALOCARBOXYLATE)

MOLECULAR WEIGHT

	Conc. mg/ml	Solvent	M.W.	Degree of Association
BrCH ₂ COO-	14.666	C ₆ H ₆	520	1.01
(Theory - 514.3)	4.294	CH ₂ Br ₂	671	1.30
ClCH ₂ COO-	7.241	CH ₂ Br ₂	358	1.06
(Theory - 335.6)	13.295	CH ₂ Br ₂	386	1.15
	26.231	CH ₂ Br ₂	333	1.00
Cl ₂ CHCOO-	5.897	CH ₂ Br ₂	702	
(Theory - 404.6)	11.396	CH ₂ Br ₂	678	
	12.813	CH ₂ Br ₂	445	1.10
	12.813	CH ₂ Br ₂	451	1.11
	15.300	CH ₂ Br ₂	481	
	16.988	CH ₂ Br ₂	538	
	34.980	CH ₂ Br ₂	473	
Cl ₃ C-COO-	Not determined.			
Cl-C(CH ₃) ₂ COO-	15.665	C ₆ H ₆	455	1.16
(Theory - 391.7)	14.855	CH ₂ Br ₂	476	1.21

TABLE XXV

INFRARED SPECTRA FOR DIMETHYLTIN BIS(MONOCHLOROACETATE).

CHCl ₃	KBr	Nujol
1790 vw		
1760 <u>sh</u>		
1735 w	1735 m, br	
	1678 m-s	1678 w
1655 <u>sh</u>		
1635 s		
1620 <u>sh</u>	1612 s	1618 s
1600 <u>sh</u>		1510 vw
	1418 m	
1405 m-s	1408 <u>sh</u>	1412 s
		1385 <u>sh</u>
1370 s		1380 s
	1342 m	1348 <u>sh</u>
	1248 m	1240 s
	1228 ms	
	1195 w	
		952 vw
	930 w	928 w
	783 m-s	788 s
		700 m
	678 w	
	636 m	635 vw
		600 vw
585 m	590 w-m	585 w-m
	580 <u>sh</u>	
532 w	532 w	533 w-m
508 w	512 m	500 w-m, br.
	485 w	

TABLE XXVI

INFRARED SPECTRA FOR DIMETHYLTIN BIS(DICHLOROACETATE).

C_6H_{12} satd. sol'n	CHCl ₃		KBr
	1% w/v	0.5% w/v	
	1780 w	1780 w	
	1760 <u>sh</u>	1760 <u>sh</u>	
1740 w-m	1743 <u>m</u>	1745 <u>w</u>	1735 w, br.
	1665 <u>sh</u>		
1650-20 w-m	1655 <u>sh</u>		
	1645 <u>s</u>	1648 s	1640 <u>sh</u>
	1622 s	1625 s	1625 <u>s</u>
		1520 vw	
			1405 <u>sh</u>
	1390 <u>sh</u>	1390 <u>sh</u>	1382 <u>m</u>
	1365 <u>s</u>	1365 <u>s</u>	1370 <u>sh</u>
	1335 <u>sh</u>		1348 <u>w-m</u>
		1235 w	
			1212 w-m
		1180 w	1195 <u>sh</u>
	1115 w	1120 w	
	945 w	950 w	
		925 w	
	820 s	820 m-s	818 w-m
			775 w-m, br.
			718 m
			665 vw
			632 w-m
			583 w
			530 vw
			475 w-m
	2% 580		
	530		
	510		

TABLE XXVII

INFRARED SPECTRA FOR DIMETHYLTIN BIS(TRICHLOROACETATE)

CHCl ₃	Nujol
1775 <u>sh</u>	
1760 <u>sh</u>	
1755 <u>sh</u>	
1745 <u>m</u>	
1705 <u>sh</u>	
1695 <u>sh</u>	
1692 <u>sh</u>	
1680 <u>s</u>	1685 vs
1655 <u>sh</u>	
1650 <u>sh</u>	1652 s
1635 <u>vs</u>	1635 <u>sh</u> , br.
	1510 vw
1400 <u>sh</u>	1390 w
1375 <u>sh</u>	1370 m-s
1362 <u>s</u>	
1335 vs	
1320 <u>sh</u>	1325 vs
1310 <u>sh</u>	1312 s
1305 <u>sh</u>	1305 m-s
	1208 vw
	1195 w
1142 w-m	
1040 w	
1028 vw	
1018 w	
960 w-m	955 w-m
	935 w
	845 s
838 vs	830 vs
	805 <u>sh</u> , br.
	748 m
	732 m
	680 s
	675 s
635 m	
	588 w
575 w	578 <u>sh</u>
	552 <u>m</u>
522 vw	528 vw
505 w	
	485 m
440 w	

TABLE XXVIII

INFRARED SPECTRA FOR DIMETHYLTIN BIS(MONOBROMOACETATE)

CHCl ₃	CHCl ₃ /C ₆ H ₁₂ 1/1	Nujol
1770 w	1772 w	
1725 w	1725 w	
		1670 <u>sh</u>
		1655 <u>sh</u>
	1635 <u>sh</u>	
1620 s	1620 s	1620 sh
		1615 <u>sh</u>
		1602 s
1592 <u>sh</u>	1592 m	1590 <u>sh</u>
		1585 <u>sh</u>
		1575 <u>sh</u>
1430 <u>sh</u>		
1400 m	1398 m	1400 w
1372 <u>sh</u>		1375 vs
1368 <u>sh</u>	1365 <u>sh</u>	1365 vs
1358 s	1360-50 s	
		1210 s
		1202 s
1180 w, br.	1190 w-m	
1012 w	1110 w	
1008 w		
950 vw	947 w	950 w
		943 w
920 vw		
890 w	888 m	888 m
		805 w-m, br.
		730 <u>sh</u>
		720 s
	695 m, br.	695 <u>sh</u>
	640 m	
	575 w-m	585 w-m
	525 vw	530 w-m
	500 w	
		460 m, br.

XXVIII respectively. Dimethyltinbis(2-chloro-2-methyl propionate) data is given in Table XXIX. These compounds, with the exception of dimethyltinbis(trichloroacetate), may reveal considerable information regarding the geometry of the carboxylate moiety. If uncoordinated carboxylate groups are present in solution or in the solid state it is entirely reasonable to expect the appearance of multiple asymmetric $\text{-CO}_2\text{-}$ stretching vibrations, indicative of conformational isomers, as has been found to occur with trialkyltinhaloacetates (43, 44).

Carbonyl-Carboxyl Region.

Solid state spectra are generally characterized by a strong absorption in the $1600\text{-}1655\text{ cm}^{-1}$ region. The electron withdrawing influence of the halogen atom is readily identified by the increased asymmetric $\text{-CO}_2\text{-}$ stretching frequency with increased electron withdrawing power of the halo substituted alkyl group ($\text{Br-CH}_2\text{COO-}$, 1602 cm^{-1} ; $\text{Cl-CH}_2\text{COO-}$, 1612 cm^{-1} ; $\text{Cl}_2\text{CHCOO-}$, 1625 cm^{-1} ; $\text{Cl}_3\text{CCOO-}$, 1652 cm^{-1}). Although some of these absorptions occur in a region normally associated with free ester-type carboxyl groups, in this case they are roughly equivalent to the absorptions observed in the trimethyltin halocarboxylate analogues.

Absorptions believed to be associated with nearly normal ester type $\text{-CO}_2\text{-}$ linkages are observed for all but the bis dichloroacetate (1670 cm^{-1} , shoulder - $\text{Br-CH}_2\text{COO-}$; 1678 cm^{-1} peak - $\text{ClCH}_2\text{COO-}$; 1685 cm^{-1} peak - $\text{Cl}_3\text{CCOO-}$). It is of particular interest that the 1685 cm^{-1} peak observed in the bistrichloroacetate compound is of greater intensity than the 1652 cm^{-1} peak, suggestive of a possible steric effect. Additionally a shoulder at 1635 cm^{-1} is also believed to be due to some type of asymmetric $\text{-CO}_2\text{-}$ stretching vibration.

TABLE XXIX

INFRARED SPECTRA FOR DIMETHYL TIN BIS(2-CHLORO-2-METHYL-PROPRIONATE)

2-Chloro-2-methylpropionic acid	CHCl ₃	C ₆ H ₁₂
1752 m	1750 vw	1750 m
1717 s		1730 m-s
		1665 <u>sh</u>
		1655 <u>sh</u>
		1645 <u>sh</u>
	1630 s	1635 <u>vs</u>
1598 w	1600 s	1610 m-s, sh
1460 w-m	1470 m	
	1420 m	
1410 w	1400 m-s	1405 s
1387 w		
1370 w	1375 m-s	1370 s
	1355 m-s	
		1300 w
1285 w-m		
1195 <u>sh</u>		1195 s
1175 m	1180 w-m, br	
1130 <u>sh</u>		
1128 m	1125 m	1125 s
		940 w-m, br
920 w	930 w-m, vbr.	
908 w		
		790 m-s
		765 m
		725 <u>sh</u>
		695 m-s
648 w	645 w-m	650 w-m
625 <u>sh</u> , br.		
	580 w-m	580 m-s
	530 vw	525 w
	505 w	505 w

All solution spectra contain a strong absorption in the 1620-1635 cm^{-1} region. This absorption is the only distinct peak present in the CHCl_3 solution spectra of dimethyltinbis(monobromoacetate). A shoulder at 1592 cm^{-1} in the chloroform solution spectra appears as a distinct peak in 1/1 $\text{CHCl}_3\text{-C}_6\text{H}_{12}$. The principle absorption again occurs at 1620 cm^{-1} preceeded by a new shoulder at 1635 cm^{-1} . Shoulders preceeding and following the strongest absorption (1635 cm^{-1}) are also present in the monochloro analogue.

Dimethyltinbis(dichloroacetate) solution spectra appear to indicate conformational effects due to the presence of two strong absorptions, 1645 and 1622 cm^{-1} . Both of these absorptions are believed due to some form of associated $\text{-CO}_2\text{-}$ group as similar absorptions are observed in the spectra of trimethyltinbisdichloroacetate (1652 cm^{-1} , CCl_4 ; 1620 cm^{-1} , Halo oil). These absorptions are not due to conformational effects of an ester-like CO_2 group as the cis and gauche $\text{-CO}_2\text{-}$ absorptions should be observed in the 1708-1687 cm^{-1} region.

Dimethyltinbis(trichloroacetate) spectra also exhibit two presumably asymmetric $\text{-CO}_2\text{-}$ stretching absorptions (1680 and 1635 cm^{-1}). The frequencies of these absorptions are believed to be of considerable significance. The 1689 cm^{-1} peak is approximately 20-25 cm^{-1} lower than would be expected for a normal ester-like $\text{-CO}_2\text{-}$ absorption (1700-1705 cm^{-1}) and about 30 cm^{-1} higher than expected (1645-1650 cm^{-1}) for a presumably symmetrically bridged carboxylate group (43). Similarly the 1635 cm^{-1} peak is about 15 cm^{-1} lower than any previously reported associated trichloroacetate group. Why the lower frequency (1635 cm^{-1}) band should appear as only a shoulder in the solid state where associated species should be more abundant and yet

be the most intense absorption in CHCl_3 solution where non-associated species should abound, is very puzzling. Also, the intensities and shapes of the absorptions in the solid state spectra are essentially the opposite of that in solution spectra. No explanation is readily apparent for this phenomenon.

It seems reasonable to assign the 1635 cm^{-1} band to a fully bridged carboxylate group and the 1680 cm^{-1} band to a partially associated carboxylate group analogous to the $1600\text{-}1610\text{ cm}^{-1}$ absorption observed in the non-halogenated bis carboxylates.

DIMETHYLTIN BIS(2-CHLORO-2-METHYL PROPIONATE)

Dimethyltin bis(2-chloro-2-methyl propionate) CHCl_3 solution spectra contain two strong absorptions (1630 and 1600 cm^{-1}). Lack of an absorption at 1717 cm^{-1} indicates the sample is free of carboxylic acid and correspondingly should be free of hydrolysis/condensation product tetramethyl 1,3-bis(2-chloro-2-methyl propionate) distannoxane. Assignment of these absorptions is far from certain. The 1600 cm^{-1} peak may be due to a bridging species as it is only $10\text{-}20\text{ cm}^{-1}$ higher frequency than the presumably unambiguous bridging carboxyl group in trimethyltin carboxylates. Electron withdrawal by the α -chlorine may account for the frequency increase. The 1630 cm^{-1} band is too high for a fully bridged carboxylate group and too low for a normal ester-like unassociated carboxyl group. It is assumed therefore, that it is similar to the $1600\text{-}1630\text{ cm}^{-1}$ band observed in the non-halogenated dimethyltin dicarboxylates: namely, associated but not "bonded" to a tin atom either intra- or inter-molecularly.

In contrast to the two strong peaks observed in CHCl_3 , only one

strong peak is observed in cyclohexane, 1635 cm^{-1} . Free carboxylic acid, presumably formed by hydrolysis, is indicated by a medium-strong absorption at 1730 cm^{-1} . Numerous shoulders preceeding the 1635 cm^{-1} absorption as well as a pronounced shoulder following it (1610 cm^{-1}) may be indicative of a multitude of species of varying geometry present in the solution. Conformational isomers, cis, gauche and bridged species, may account for the complexity; however, examination of molecular models reveals cis and gauche isomers are an unlikely explanation.

Tin-Carbon Stretching Region.

Non-linear geometry seems indicated for the C-Sn-C skeleton in all five compounds both in solution and in the solid state. Spectra of each compound contain two absorptions which are believed to be due to asymmetric ($570\text{-}590\text{ cm}^{-1}$) and symmetric ($520\text{-}530\text{ cm}^{-1}$) tin-carbon stretching modes.

NMR Spectra.

NMR parameters for dimethyltin bis(monobromoacetate), dimethyltin bis(monochloroacetate), dimethyltinbis(dichloroacetate), dimethyltinbis(trichloroacetate) and dimethyltinbis(2-chloro-2-methylpropionate) are given in Tables XXX, XXXI, XXXII and XXXIII.

Dimethyltinbis(monobromoacetate) is characterized by resonances at 8.82 and 6.00τ due to $\text{CH}_3\text{-Sn}$ and $\text{Br-CH}_2\text{-}$ protons respectively. Spin-spin couplings ($J=81.6\text{ cps}$) are associated with the 8.82τ resonance. Minor intensity resonances at 8.94 and 9.05τ are believed to be due to methyl groups on tin in the hydrolysis/condensation product tetramethyl-1,3-bis(monobromoacetoxo)distannoxane.

TABLE XXX

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTINBIS(MONOBROMOACETATE)

Solvent	Conc. mg/ml	Temp. °C	CH ₃ -Sn τ	J ¹ cps	J ² cps	Br-CH ₂ -COO τ	
CDCl ₃	250	R.T.	8.82	81.6	78.3	6.00	(a)
CDCl ₃		+55	8.84	82.5	78.0		(b)
CDCl ₃		0	8.79	82.7	79.1		(b) (c)
CDCl ₃		-30	8.75	83.5	79.6		(b) (d)
CDCl ₃		-50	8.72	84.6	80.3		(b) (e)

(a) External TMS, A-60 spectrometer.

(b) External TMS, A56-60A spectrometer.

(c) Impurities 8.93 and 9.03 τ .

(d) Impurities 8.90 and 9.00 τ .

(e) Impurities 8.89 and 8.99 τ .

TABLE XXX CONT.

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTINBIS(MONOBROMOACETATE)
D₂O ADDED.

Solvent	Temp. °C	CH ₃ -Sn τ	J ¹ cps	J ² cps	
CDCl ₃	+55				
CDCl ₃	41	8.85			
CDCl ₃	0	8.87	85.8	82.5	
CDCl ₃	-30	8.78	86	82	
CDCl ₃	+55	8.96	≈ 93		(a)
CDCl ₃	41	8.94	94.5	90.2	(a)
CDCl ₃	0	8.99	93.0	89.3	(a)
CDCl ₃	-30	8.93	95	90	(a)
CDCl ₃	+55	9.06	90		(a)
CDCl ₃	41	9.06	89.8	85.6	(a) (b)
CDCl ₃	0	9.10	88.8	84.8	(a) (c)
CDCl ₃	-30	9.04	89	84.5	(a) (d)

(a) Methyl group of tetramethyl-1,3-bis(monobromoacetoxymethyl)distannane.

(b) Impurity 9.90 τ.

(c) Impurity 9.98 τ.

(d) Impurity 9.93 τ.

TABLE XXXI

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTINBIS(MONOCHLOROACETATE)
AND DIMETHYLTINBIS(DICHLOROACETATE).

$\text{Me}_2\text{Sn}(\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{R})_2$	Solvent	Conc. mg/ml	Temp. °C	CH_3-Sn τ	J^1 cps	J^2 cps	$\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{R}$ τ
R = H_2ClC	CDCl_3		31	8.79 (a)	80.9	77.2	5.80
R = HCl_2C	CDCl_3	165	31	8.72 (b)	79.2	75.6	4.04

(a) Impurity 8.94 and 9.02 τ .

(b) Impurity 8.85 and 8.96 τ .

TABLE XXXII

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTINBIS(TRICHLOROACETATE).

Solvent	Conc. mg/ml	Temp. °C	CH ₃ -Sn τ	J ¹ cps	J ² cps	Impurities τ
CDCl ₃	≈890	R.T.	8.62	82.6	78.8	8.78, 8.87
CDCl ₃	≈410	R.T.	8.59	83.7	80.4	8.73, 8.81
CDCl ₃	≈300	R.T.	8.57	81.5	78.0	9.16(a)
CDCl ₃		R.T.	8.60	82.3	78.5	9.17(b)
CDCl ₃ C ₅ D ₅ N		R.T.	8.83	≈109		9.17, 9.44
CDCl ₃		R.T.	8.57	83.5	79.8	9.13(c), 8.64

(a) Estimated concentration 6% of total.

(b) Estimated concentration 5% of total.

(c) Estimated concentration 14% of total.

TABLE XXXIII

PROTON MAGNETIC PARAMETERS FOR DIMETHYLTINBIS(2-CHLORO-2-METHYL-
PROPIONATE).

Solvent	Conc. mg/ml	Temp. °C	CH ₃ -Sn τ	J ¹ cps	J ² cps	Cl-(CH ₃) ₂ -COO- τ	
CDCl ₃		R.T.	8.87	83.0	79.3	8.11	(a)
CDCl ₃ C ₅ D ₅ N		R.T.	9.23	108	102.9	8.43	(a)
CDCl ₃	≈175	55	9.13	82.9	79.1	8.38	(b)
CDCl ₃	≈175	40	9.13	82.7	79.2	8.38	(b)
CDCl ₃	≈175	R.T.	9.12	82.8	79.1	8.38	(b)(c)
CDCl ₃	≈175	0	9.13	83.5	79.6	8.38	(b)
CDCl ₃	≈175	-30	9.13	83.1	79.6	8.38	(b)

(a) External TMS, A-60 spectrometer.

(b) Internal TMS, HA-100 spectrometer.

(c) Impurities 9.21 and 9.33 τ .

Variable temperature studies over the range $+55^{\circ}$ to -50°C reveal a decrease in the chemical shift of the methyl groups on tin and a small increase in the magnitude of J as the temperature is lowered (Table XXX).

Confirmation of the assignment of the 8.94 and 9.05 τ resonances to hydrolysis/condensation product tetramethyl-1,3-bis(monobromoacetate)distannoxane is provided by the results of adding D_2O to the CDCl_3 solution. Resonances in the 8-10 τ region at 8.85, 8.94 and 9.06 τ are essentially identical to those observed prior to adding D_2O . Significantly, the 8.85 τ resonance is now very weak in relation to the signals at 8.94 and 9.06 τ , and the spin-spin couplings are too diffuse and too weak to allow meaningful measurement. In contrast, the higher field resonances exhibit clear spin-spin couplings (8.94 τ , $J=94.5$ cps; 9.06 τ , $J=89.8$ cps). Additionally, a new impurity peak believed to originate with a methyltin species, is observed at 9.90 τ .

Variable temperature studies of the D_2O added sample clearly indicate an equilibrium between the hydrolysis product and dimethyltinbis(monobromoacetate). Increasing the sample temperature to $+55^{\circ}\text{C}$ results in disappearance of the 8.85 τ resonance, an increase in intensity of the 8.96 τ resonance with considerable broadening of the signal, and a decrease in intensity of the 9.06 τ signal with signal broadening. Decreasing the temperature to 0°C results in three clear signals each of which has a relatively clear set of coupling constants (8.87 τ , $J=85.8$ cps; 8.99 τ , $J=93.0$ cps; 9.10 τ , $J=88.8$ cps).

Signal intensities of the 8.99 and 9.10 τ resonances are now the reverse of that observed at $+55^{\circ}\text{C}$, i.e. the 9.10 τ resonance is now

more intense than the 8.99 τ resonance. The change in signal intensity with temperature is consistent with observations previously reported for other distannoxane systems (69).

Dimethyltinbis(monochloroacetate) and dimethyltinbis(dichloroacetate) were not examined as extensively as the monobromo analogue. However, based on the available data (Table XXXI), the compounds not surprisingly appear to be essentially isostructural with dimethyltinbis(monobromoacetate), as all of the NMR parameters are essentially identical.

A methyltin resonance at 8.62 τ ($J=82.6$ cps) assignable to the methyl group protons of dimethyltinbis(trichloroacetate) and much less intense resonances at 8.78 and 8.87 τ assignable to the methyl group protons of tetramethyl-1,3-bis(trichloroacetoxy)distannoxane characterize the NMR spectrum of dimethyltinbis(trichloroacetate) as obtained in this study. The species in solution does not appear to be appreciably concentration dependent, as the magnitude of J decreases only slightly with decreasing concentration (Table XXXII). In view of the greater electronegativity of a trichloroacetate group in relation to the other haloacetates, a slightly larger J value is to be expected, and indeed the value of 82.6 cps is the largest obtained. Judging by the similarity in magnitude of J , dimethyltinbis(trichloroacetate) is believed to be structurally similar to the other dimethyltinbis(haloacetate) compounds discussed previously.

As will be readily evident, dimethyltinbis(2-chloro-2-methylpropionate) appears to differ significantly from the dimethyltinbis(haloacetate) compounds in at least one significant respect. Room temperature NMR spectra contain resonances at 8.87 and 8.11 τ in a

ratio approaching 1:2 with the former peak having symmetrically disposed spin-spin couplings ($J=83.0$ cps). Assignment of the 8.87τ resonance to the $\text{CH}_3\text{-Sn}$ protons and the 8.11τ resonance to the methyl protons of the carboxylate moiety is relatively certain.

Variable temperature studies revealed essentially no change in the chemical shifts or coupling constants with increased or decreased temperature. This behavior is to be contrasted with that observed for the non-halogenated dicarboxylates and the monobromoacetate analogue. No explanation for this phenomenon is readily apparent.

Complex Formation Studies.

Addition of pyridine- d_5 to dimethyltin-bis(monobromoacetate), -bis(monochloroacetate) and -bis(dichloroacetate) resulted in the formation of a white solid material. No attempt was made to isolate or characterize these materials.

Dimethyltinbis(trichloroacetate) also forms a white solid on adding pyridine- d_5 . However, in this case attempts were made to isolate and characterize this material. Examination of the filtered CDCl_3 solution revealed a pronounced resonance at 8.83τ with couplings ($J \approx 109$ cps) as well as two less intense resonances at 9.17 and 9.44τ . Due to the low intensity of the signals couplings could not be determined. Assignment of the 8.83τ resonance to complexed dimethyltinbis(trichloroacetate) is reasonable in view of the location of the signal and the magnitude of the observed couplings. The 9.17τ resonance may be due to trimethyltin trichloroacetate impurity as a peak at 9.13τ with couplings ($J=59$ cps) was observed in a spectrum of uncomplexed and impure dimethyltinbis(trichloroacetate).

No assignment is offered for the 9.44 τ resonance other than that the location suggests it is due to some type of trimethyltin species.

Examination of an acetone- d_6 solution of dimethyltinbis(trichloroacetate) pyridine adduct (prepared by adding an excess of pyridine to the compound in $CHCl_3$ followed by removal of excess pyridine and $CHCl_3$ at high vacuum) indicated by integration that the adduct was indeed the anticipated 1:2 (compound:pyridine) complex.

The area of the spectrum in which methyltin resonances normally occur is very complex, suggesting a multitude of methyltin species are present.

No white solid forms on adding pyridine- d_5 to a $CDCl_3$ solution of dimethyltinbis(2-chloro-2-methyl propionate). The coupling constant J increases to 108 cps and the methyltin and methylpropionate resonances shift upfield to 9.23 and 8.43 τ respectively. The increased magnitude of J suggests that the species present is of significantly different geometry and/or coordination state than the uncomplexed material.

Structural Implications.

The low degree of association indicated by the molecular weight studies, rather unusual $-CO_2-$ stretching frequencies, and both asymmetric and symmetric Sn-C stretching frequencies observed in the infrared spectra, and relatively constant values of J between 80-84 cps are consistent with the distorted octahedral, long "bonded" structure previously proposed for the non-halogenated dimethyltin dicarboxylates.

EXPERIMENTAL

Dimethyltin Oxide.

Excess ammonium hydroxide was added to a water solution of dimethyltin dichloride. Copious quantities of white curdy insoluble product formed immediately. The mixture was stirred about 1/2 hour, suction filtered, washed with water until free of chloride ion and dried in a CaCl_2 vacuum dessicator. Final drying prior to use was achieved by applying high vacuum for several hours.

The dimethyltin oxide used in some preparations resulted from the decomposition of trimethyltin hydroxide during sublimation.

Dimethyldivinyltin.

The method of Seyferth and Stone (70) was used with modifications:

Equipment: Five liter 3 neck flask, dry ice condenser, 500 ml pressure equilizing dropping funnel, teflon stirring blade, ground glass stirring shaft assembly, electric stirring motor, nitrogen system with bubbler, electric heating mantle.

Reagents: Tetrahydrofuran (THF, Dupont) was refluxed 16 hours with LiAlH_4 and freshly distilled prior to use.

Vinyl bromide (Matheson) was liquified prior to use by means of a dry ice condenser.

Magnesium turnings (Mallinckrodt, Grignard grade) were baked 36 hours at 140°C and used as soon as cool.

Dimethyltin dichloride (M&T) was used as received.

Other materials were readily available.

Procedure: Magnesium turnings (10.6 g) were placed in the flask, and the entire system thoroughly flamed with dry N_2 passing through

the system. A continuous stream of nitrogen was passed through the system during cooling. Vinyl bromide (25 ml) in THF (50 ml) was added and stirring begun. After 15 minutes stirring a sudden, vigorous reaction started as indicated by foaming and an immediate color change from colorless to dirty green-brown. THF (\approx 200 ml) and the remaining magnesium turnings (19.8 g) were added. Vinyl bromide (\approx 50 ml) in THF (200 ml) was added dropwise at a rate sufficient to maintain steady reflux. An additional quantity of vinyl bromide (\approx 30 ml) in THF (150 ml) was required to consume all of the magnesium. Total addition time was about 3 1/2 hours.

A Freidrichs condenser was substituted for the dry ice condenser and the reaction refluxed about 20 minutes to remove excess vinyl bromide.

Dimethyltin dichloride (109.3 g, 0.5 mole) dissolved in 300 ml THF was added at a rate sufficient to maintain steady reflux. External heating was begun upon completion of the addition, and the reaction refluxed 19 hours. After cooling, the reaction mixture was hydrolyzed with 250 ml of saturated NH_4Cl solution (added dropwise) and the THF layer decanted through a glass wool plug. Laboratory ether (\approx 250 ml) was added to the tan curdy salts remaining in the flask followed by an additional 300 ml of saturated NH_4Cl solution. A rather pasty mass formed in the flask. A yellow-brown ether layer and a yellowish water layer formed after adding water (700 ml). The layers were separated by a black, spongy-looking interface approximately two inches thick.

The ether layer was separated via separatory funnel, the water layer washed twice with ether, the ether and THF solutions combined

and dried over CaCl_2 .

Solvent was removed through a 30-inch glass helix-packed vacuum-jacketed distilling column fitted with a fraction cutting distilling head.

The liquid remaining after solvent removal was fractionated through an 18-inch vigreux column to yield three fractions.

1. B. P. 116-121°C 57.34 g.

2. B. P. 121-125°C 24.30 g.

3. B. P. 126-165°C 8.84 g.

Lit. (70) B. P. 118-120°C.

NMR examination confirmed the identification of the material as dimethyldivinyltin.

2-Chloro-2-methylpropionic Acid.

No really satisfactory method of preparation was found for 2-chloro-2-methylpropionic acid. Low yields ($\approx 25\%$) were obtained via use of the Hell-Volhard-Zelinski reaction. The following preparations are representative of the methods attempted.

Equipment: Three-neck 100 ml flask, Freidrichs condenser, gas inlet tube, serum capped injection port, steam bath, safety flasks for gas system.

Reagents: Isobutyric acid (Eastman), chlorine gas (Matheson), PCl_3 (obtained from Mr. Roger Gay).

Procedure:

A. Isobutyric acid (50 ml) was put into the flask and heated on the steam bath. Chlorine was bubbled through the acid and about 2 ml PCl_3 was added through the injection port. Additional PCl_3 (1 ml) was added after 30 minutes and again after 1 hour heating. Continued

heating and passing chlorine through the liquid for a total of 8 hours.

After cooling, the dissolved chlorine was removed by aspirator vacuum and subsequently, the brown-black residue was stripped of all volatile material by aspirator vacuum distillation.

Water (2-3 ml) was added to the distillate to destroy any acid chloride which may have been present, and the material vacuum fractionated through a spinning band column. Unfortunately, the distillate attacked the metal of the spinning band and destroyed it. The only product obtained, other than unreacted isobutyric acid, was a clear, lemon-yellow liquid, B.P. 69-79°C at 18-20 mm Hg. Subsequent NMR examination indicated the material was 2-chloro-2-chloromethyl propionic acid (CH_3 - 8.15 τ ; ClCH_2 - 6.39, 6.20, 6.00, 5.81 τ ; COOH - 2.53 τ ; theoretical ratio 3.0:2.0:1.0; experimental ratio: 2.98:1.98:1.0).

B. Thionyl chloride (SOCl_2 59.5 g; 0.5 mole) was added dropwise to magnetically stirred isobutyric acid (44 g, 0.5 mole) in a 100 ml three-neck flask fitted with a Freidrichs condenser connected to an oil bubbler and heated by an electric mantle. After gas evolution had stopped, PCl_3 (1 ml) was added and chlorine was bubbled through the liquid for 4 hours. Water (9 ml) was added to hydrolyze the acid chloride, and the mixture was distilled through a 16-inch Vigreux column using aspirator vacuum. Three fractions were obtained.

1. B.P. 60-65°C @ \approx 12 mm 50%.
2. B.P. 65-83°C @ \approx 12 mm 30%.
3. B.P. 83-86°C @ \approx 12 mm 20%.

Fraction three solidified on reaching the receiver. Due to

carelessness the receivers were not preweighed, thus the distribution among the fractions was estimated.

C. Chlorine was bubbled through isobutyric acid (46 ml) while warming it to 80-100°C. On adding PCl_3 (3 ml) to the brilliant yellow liquid, the color disappeared immediately. A black, opaque liquid was present after passing chlorine through the mixture for 6 hours. Vacuum distillation of the residue through a 16 inch Vigreux column yielded two fractions.

1. B.P. 60-65°C @ 10-12 mm.

2. B.P. 84-86°C @ 10-12 mm.

Fraction 2 amounted to about 25% of the expected volume and solidified in the receiver.

Fractions B3 and C2 were combined, and the material recrystallized using CHCl_3 . The recrystallized material was a mixture of a mushy semi-solid and a clear liquid at room temperature; therefore, identification was achieved by NMR examination rather than melting point Lit. (31°C) (71).

Dimethyltin diformate.

A. Excess formic acid (20 ml, 98%) was added to dimethyltin oxide (21.918 g) and the mixture refluxed about two hours. Removal of unreacted formic acid by aspirator vacuum distillation, and sublimation of the residue resulted in 4.9744 g of white solid product.

The sublimate was recrystallized from hot concentrated formic acid with cooling in a refrigerator, filtered through a sintered glass funnel and dried 12 hours at less than 0.1 mm Hg in a CaCl_2 vacuum dessicator; yield 3.617 g shiny white flakes. [Found:

C, 20.24; H, 3.42; O, 27.04. $C_4H_8O_4Sn$. Calcd: C, 20.11; H, 3.35; O, 26.81%.] Molecular weight calcd: 238.7; found: 911 (5.829 mg/ml CH_2Br_2).

B. Dimethyltin oxide (2 g) and formic acid (0.9 ml, 98%) were refluxed approximately 20 minutes. All of the dimethyltin oxide dissolved. Excess formic acid and water of reaction were removed under high vacuum and the residue sublimed directly from the flask onto a water cooled condenser. The flask was immersed in an oil bath heated to $140^\circ C$ during sublimation. The sublimate (≈ 2.5 g) was resublimed at high vacuum using a $95^\circ C$ oil bath and a water cooled condenser; 2.490 g of snow-white material was obtained. [Found: C, 21.04; H, 3.05; O, 26.05. $C_4H_8O_4Sn$. Calcd: C, 20.11; H, 3.35; O, 26.81%.]

Dimethyltin diacetate.

The following experiments are considered representative of the many attempts to prepare dimethyltin diacetate.

A. Acetic anhydride/acetic acid (25 ml) was refluxed with dimethyltin oxide (4.2 g, obtained from decomposition of trimethyltin hydroxide, non-volatile at $150^\circ C$ and high vacuum), two hours and the excess acetic anhydride/acetic acid removed by aspirator-vacuum distillation. The dark crystalline residue was sublimed directly from the flask onto an ice/water cooled condenser resulting in 2.70 g of white, crystalline sublimate, smelling strongly of acetic acid.

The sublimate was dissolved in a mixture of ethyl acetate/acetic anhydride/acetic acid and the volume reduced to about 1/3. Cold pentane was added, and the material cooled in a refrigerator. Filtration of the cooled mixture recovered 1.389 g of white, crystalline material which was dried in a vacuum dessicator. [Found: C, 23.01; H, 4.34;

O, 15.20. $C_6H_{12}O_4Sn$. Calcd: C, 27.0; H, 4.50; O, 24.0%.] Trimethyltin formate appeared to have formed; Calcd. for $C_4H_{10}O_2Sn$: C, 23.0; H, 4.79; O, 15.33%.

B. Glacial acetic acid (15 ml) was refluxed about 4 hours with dimethyltin oxide (2 g). The excess acid was removed by distillation and the residue sublimed twice at high vacuum. [Found: C, 23.13; H, 4.43; O, 16.49. $C_6H_{12}O_4Sn$. Calcd: C, 27.0; H, 4.50; O, 24.0%.]

C. Acetic anhydride (6 ml), dimethyltin oxide (4.89 g) and sodium dried benzene (25 ml) were refluxed about 16 hours. A slow stream of nitrogen was passed through the system during reflux. Benzene and excess acetic anhydride were removed by distillation with a slow stream of nitrogen passing through the system.

The reaction flask was attached to the high vacuum system through a sublimator and full high vacuum applied for one half hour to ensure removal of benzene and acetic anhydride. Water was then circulated through the sublimator condenser. A small amount of white solid formed on the condenser during the following three hours. The sublimator was transferred to a dry-nitrogen-filled glove bag, and the small amount of sublimate removed. Subsequent NMR examination indicated the sublimate was the desired product.

Dichloromethane was added to the pale yellow, needle-like mass in the reaction flask. Sodium-dried petroleum ether was added and the clear yellow solution allowed to evaporate inside the nitrogen-filled glove bag.

Filtration of the crystalline material, formed on solvent evaporation, produced a white, crystalline solid. The material was allowed to dry in the glove bag. A glass ampoule was filled in the

glove bag, sealed and submitted for analysis. [Found: C, 24.02, 24.10; H, 4.49, 4.65; O, 17.88, 17.75. $C_6H_{12}O_4Sn$. Calcd: C, 27.0; H, 4.50; O, 24.0%.] An intense orange-yellow mother liquor remained.

Dimethyltin dipropionate.

A. Propionic acid (1.8 ml, 1.82 g, ≈ 0.0246 mole) was added to dimethyldivinyltin (2 ml, ≈ 2.5 g, ≈ 0.0123 mole) in a thoroughly dried, 50 ml round-bottom flask fitted with a water cooled condenser topped with a $CaCl_2$ drying tube. The reaction was heated until the acid began to reflux. Dichloromethane was added to the solid, crystalline mass which formed on cooling, and the solution filtered in a system protected from moisture. Pentane was added to the filtered solution and the solution placed in a freezer. Filtration of the resulting solid followed by recrystallization from pentane resulted in a material contaminated with a trimethyltin species (NMR). Subsequent room temperature high vacuum sublimation with a water cooled condenser produced a small amount of white sublimate which was discarded. The white, crystalline residue was submitted for analysis. [Found: C, 28.24; H, 5.22; O, 14.10. $C_8H_{16}O_4Sn$. Calcd: C, 33.04; H, 4.13; O, 22.01%.]

B. Propionic acid (7.76 g, 0.105 mole), dimethyltin oxide (4.312 g, 0.026 mole) and benzene (40 ml) were placed in a 100 ml flask equipped with a Dean-Stark azeotropic distillation trap, condenser and $CaCl_2$ drying tube. Benzene was distilled from the reaction after 24 hours reflux. High vacuum sublimation at 50°C produced a considerable quantity of white, crystalline sublimate. Residue in the flask consisted of an oil and crystals. Recrystallization of the residue and sublimation failed to remove a small quantity of free

propionic acid as indicated by IR examination (band at 1712 cm^{-1}).

The initial sublimate was submitted for analysis. [Found: C, 30.10, 30.27; H, 5.50, 5.37; O, 18.39, 18.35. $\text{C}_8\text{H}_{16}\text{O}_4\text{Sn}$. Calcd: C, 33.04; H, 4.13; O, 22.01%.]

Dimethyltin diisobutyrate.

A. Isobutyric acid (4 ml) was refluxed about 1 hour with dimethyltin oxide (1.17 g). Excess isobutyric acid was removed by vacuum distillation, and the yellowish-white solid subjected to high vacuum room temperature sublimation. Using a water cooled condenser, the vast majority of residue formed a white crystalline sublimate. [Found: C, 34.91; H, 6.22; O, 11.41. $\text{C}_{10}\text{H}_{20}\text{O}_4\text{Sn}$. Calcd: C, 37.19; H, 6.20; O, 19.83%.]

B. Isobutyric acid (2.3 ml, ≈ 0.0246 mole), dimethyldivinyltin (2 ml, ≈ 0.0123 mole) and dichloromethane (10 ml) were combined in a 50 ml flask previously flamed with nitrogen streaming through the flask, and protected from moisture during cooling. The reaction mixture was stirred magnetically 4 hours, and then heated to remove some of the dichloromethane and ensure reaction. Excess acid and solvent were removed by distillation under nitrogen. Room temperature high vacuum sublimation of the white crystalline residue produced a small quantity of white sublimate during 12 hours pumping. The sublimer was transferred to a nitrogen-filled glove bag protected with P_2O_5 , the sublimate removed, the sublimer condenser cleaned and the apparatus reassembled. The vast majority of the remaining residue sublimed onto a water cooled probe when heated to 77°C (oil bath). [Found: C, 35.64, 35.44; H, 6.44, 6.26; O, 16.92, 16.74. $\text{C}_{10}\text{H}_{20}\text{O}_4\text{Sn}$. Calcd: C, 37.19; H, 6.20; O, 19.83%.]

C. Isobutyric acid (3.4 ml, \approx 0.037 mole) and dimethyldivinyltin (3 ml, \approx 0.0185 mole) were combined in a 50 ml flask protected from moisture, heated to 57°C (oil bath) and stirred magnetically two days. The temperature was increased to 80°C for 24 hours and further increased to 110°C for an additional three days. Long, white needle clusters formed on cooling. Room temperature high vacuum sublimation (24 hours) produced a small amount of white sublimate. The sublimer assembly was transferred to a nitrogen filled glove bag protected with P_2O_5 , the sublimate removed from the condenser, the condenser cleaned and the apparatus reassembled. Continued high vacuum sublimation at 80°C (oil bath) again produced a white solid sublimate. The glove bag procedure was repeated and the sublimate submitted for analysis. [Found: C, 36.10; H, 6.09; O, 18.40. $C_{10}H_{20}O_4Sn$. Calcd: C, 37.19; H, 6.20; O, 19.83%.] M.P. 68-70°C (Gallenkamp apparatus, sealed capillary).

Continued high vacuum sublimation at 100°C produced a vast quantity of white, crystalline sublimate. In fact, the sublimer became blocked due to the sublimate. The material was removed in the glove bag, a portion placed in a glass ampoule, the ampoule sealed and submitted for analysis. [Alfred Bernhardt, Found: C, 36.95; H, 6.18; O, 16.25. $C_{10}H_{20}O_4Sn$. Calcd: C, 37.19; H, 6.20; O, 19.83%.] M.P. 70-72°C (Gallenkamp apparatus, sealed capillary).

Approximately two months later, an additional sample of the above material was submitted to a different analyst. [Pascher, Found: C, 35.08; H, 6.08; Sn, 38.83. $C_{10}H_{20}O_4Sn$. Calcd: C, 37.19; H, 6.20; Sn, 36.52%.]

Dimethyltin dipivalate.

A. Dimethyltin oxide (residue from Me_3SnOH sublimation) and excess pivalic acid were refluxed about one-half hour. Excess acid was removed by aspirator vacuum distillation. Sublimation and subsequent recrystallization from hot n-hexane yielded a white, crystalline product. [Found: C, 41.76; H, 7.01; O, 12.76. $\text{C}_{12}\text{H}_{24}\text{O}_4\text{Sn}$. Calcd: C, 41.08; H, 6.84; O, 18.24%.] M.P. very broad beginning at 92°C . Molecular weight (430; 4.132 mg/ml benzene; calcd: 351).

B. Dimethyltin oxide (1.786 g, 0.0108 mole), pivalic acid (2.256 g, 0.0221 mole) and benzene were heated by an oil bath for a few minutes. A portion of the benzene was distilled resulting in a clear, colorless reaction flask. The remaining benzene was removed by distillation and spin evaporation. Ether and hexane were added to the crystalline residue and the flask heated briefly on a steam bath. The resultant milky mixture was cooled in a freezer but no solid formed. The solvents were removed by spin evaporation and the resulting solid dissolved in hot CHCl_3 . Ether was added to the pale yellow solution and the volume reduced by spin evaporation. Very little solid separated on cooling in a freezer. The recrystallization flask was attached to the high vacuum system through a sublimer. After removal of solvents, the flask was heated to 80°C (oil bath). The white sublimate was removed and the bath temperature increased to 135°C . No additional sublimate was obtained.

The sublimate was dissolved in CHCl_3 and the CHCl_3 allowed to evaporate through a small hole in the plastic capped recrystallization vial in an effort to obtain definite crystals. Beautiful, large, clear prisms were obtained after about a week to 10 days. The

pale yellow mother liquor was decanted, and the crystals washed with a minimum amount of cold pentane. [Found: C, 32.26; H, 6.10; O, 13.34. $C_{10}H_{24}O_4Sn$. Calcd: C, 41.08; H, 6.84; O, 18.24%.] M.P. 198-200°C (Gallenkamp apparatus, sealed capillary).

The above analysis is consistent with the sample containing largely hydrolysis/condensation product tetramethyl-1,3-dipivaloxy-distannoxane. $C_{14}H_{30}O_5Sn_2$ requires C, 32.61; H, 5.82; O, 15.52%.

C. Pivalic acid (2.51 g, ≈ 0.0246 mole) and dimethyldivinyltin (2.0 ml, ≈ 0.0123 mole) were combined in a 50 ml flask fitted with a condenser topped with a $CaCl_2$ drying tube. All equipment had been previously baked at least 12 hours at 140°C and allowed to cool in a $CaCl_2$ dessicator. The mixture was heated by electric mantle for 1-1 1/2 hours by which time the evolution of bubbles had stopped and the contents of the flask had changed from colorless to a clear, dark brown liquid. The contents of the flask solidified into a mass of needles on cooling. Extraction of the solid with dichloromethane, filtration of the solution through a fritted filter in a system protected from moisture and reducing the volume of liquid by applying vacuum, produced white needle crystals in the liquid. The flask was stoppered and placed in a freezer. Filtration, volume reduction and cooling produced several crops of crystalline material.

All solid materials were combined (P_2O_5 protected glove bag), the flask attached to a sublimator, and the sublimator transferred from the glove bag and attached to the high vacuum system. A small quantity of white solid was obtained after 24 hours room temperature high vacuum sublimation. The sublimation was continued at 77°C after the usual sublimate removal and condenser cleaning procedure in the glove

bag. A large quantity of white, shiny flake-like sublimate was obtained. [Found: C, 42.40; H, 7.24; O, 17.34. $C_{12}H_{24}O_4$ Sn. Calcd: C, 41.08; H, 6.84; O, 18.24%.]

Resublimation at room temperature and high vacuum resulted in a few clear, colorless, square prisms on the water condenser and white, crystalline material residue in the flask. The residue was submitted for analysis. [Found: C, 40.93; H, 6.74; O, 18.21. $C_{12}H_{24}O_4$ Sn. Calcd: C, 41.08; H, 6.84; O, 18.24%.] M.P. 90-94°C (Gallenkamp apparatus, sealed capillary). Molecular weight (380, 8.654 mg/ml CH_2Br_2 ; 377, 19.016 mg/ml CH_2Br_2 ; 357, 9.362 mg/ml benzene; 418, 17.900 mg/ml benzene. Calcd: 350.7).

Dimethyltinbis(monobromoacetate).

All equipment was thoroughly baked, cooled in a $CaCl_2$ dessicator, and the assembled apparatus flamed with nitrogen passing through the system. A continuous nitrogen atmosphere was maintained throughout the reaction.

Bromoacetic acid (3.42 g, ≈ 0.0246 mole), diluted with dichloromethane (10 ml), was added dropwise to a magnetically stirred solution of dimethyldivinyltin (2.0 ml, ≈ 0.0123 mole) diluted with dichloromethane (10 ml). The resultant mixture was stirred one hour, then heated to reflux and the dichloromethane removed by distillation. A very small amount of sublimate was obtained on room temperature high vacuum sublimation. The residue in the flask was dissolved in dichloromethane and the solution filtered in an apparatus protected from moisture. Copious quantities of long, thin, white needles formed on adding petroleum ether. The recrystallization was repeated three times in a dry nitrogen atmosphere and the material allowed to

dry in the dried nitrogen atmosphere. [Found: C, 16.77; H, 2.45; O, 14.81; Br, 37.44. $\text{Br}_2\text{C}_6\text{H}_{10}\text{O}_4\text{Sn}$. Calcd: C, 16.96; H, 2.36; O, 15.09; Br, 37.64.] Molecular weight [407, 11.229 mg/ml CH_2Br_2 ; 404, 27.135 mg/ml CH_2Br_2 ; 520, 14.666 mg/ml benzene]. M.P. 153-154°C (Gallenkamp apparatus, sealed capillary). Lit. 159-160°C (68).

Dimethyltinbis(monochloroacetate).

Dimethyltin oxide (1.725 g, 0.0104 mole), chloroacetic acid (2.318 g, 0.0245 mole) and benzene (20 ml) were heated about 15 minutes in a 160°C oil bath with occasional swirling. No extraordinary precautions were taken to ensure absence of moisture. The reaction was allowed to cool and benzene removed by spin evaporation. The solid residue was extracted with dichloromethane and hexane added to the clear solution. Copious quantities of white needles formed immediately on adding hexane. The filtered white needles were washed with hexane and dried in a vacuum dessicator attached to the high vacuum system. The vacuum was relieved by admitting dry nitrogen. [Found: C, 21.60; H, 2.80; O, 19.11; Cl, 21.24. $\text{Cl}_2\text{C}_6\text{H}_{10}\text{O}_4\text{Sn}$. Calcd: C, 21.47; H, 2.98; O, 19.07; Cl, 21.12%.] Molecular weight [358, 7.341 mg/ml CH_2Br_2 ; 386, 13.295 mg/ml CH_2Br_2 ; 333, 26.231 mg/ml CH_2Br_2]. M.P. 166-168°C (Gallenkamp apparatus, sealed capillary). Lit. 163-165°C (68). Yield: 3.125 g, 88.9% of theory.

Dimethyltinbis(dichloroacetate).

Dichloroacetic acid (0.8 ml, 1.27 g, ≈ 9.86 mmoles) was added to dimethyldivinyltin (1.01 g, 4.93 mmoles) in a 50 ml flask. A vigorous reaction occurred immediately, the flask became very hot, and the contents boiled and frothed. A solid mass formed on cooling. The

residue was dissolved in warm dichloromethane and petroleum ether added. Immediately white needle crystals formed almost filling the flask. The filtered and dried material began melting at 150°C, about 75°C below the expected range. Recrystallization from chloroform/pentane produced a white needle crystalline material. M.P. 242-245°C Lit. 226-228°C (68).

Extreme measures were taken to ensure absence of moisture. All manipulations were carried out in a P_2O_5 dried glove bag.

The initial reaction described above was carried out. The clear amber liquid present after frothing stopped solidified on cooling. The solid mass was completely soluble in dichloromethane. The solution was filtered in an apparatus protected from moisture and petroleum ether added to the clear filtrate. Large quantities of long, white needles formed on cooling in a refrigerator. The filtered needles were washed with petroleum ether, again recrystallized from dichloromethane/petroleum ether and sucked dry. The resultant mass of light, fluffy, white needles had the appearance of glass wool.

[Found: C, 17.74; H, 2.27; O, 15.96; Cl, 34.83. $Cl_4C_6H_8O_4Sn$.

Calcd: C, 17.81; H, 1.98; O, 15.82; Cl, 35.06.] Molecular weight

[445, 12.813 mg/ml CH_2Br_2 ; 451, 12.813 mg/ml CH_2Br_2 ; 481, 15.300

mg/ml CH_2Br_2 ; 538, 16.988 mg/ml CH_2Br_2 ; 678, 11.366 mg/ml CH_2Br_2 ;

702, 5.897 mg/ml CH_2Br_2 ; 473, 34.980 mg/ml CH_2Br_2].

Dimethyltinbis(trichloroacetate).

A. Trichloroacetic acid (6.841 g, 41.9 mmol) and dimethyltin oxide (1.656 g, 10.03 mmol) were heated until the acid started to boil. All of the solid disappeared and a tan solid formed on cooling the clear yellow liquid. The crystalline mass was extracted with

warm dichloromethane and the extract filtered through a fritted glass filter. The small amount of white residue on the filter disc was washed with chloroform and the washings combined with the dichloromethane filtrate. Reducing the filtrate volume by 1/2 by rotary evaporation with resultant evaporative cooling, resulted in an amorphous, white, solid precipitate. The solid was separated by filtration, washed with petroleum ether, and briefly air dried. [Found: C, 14.10; H, 1.98; O, 9.02; Cl, 40.86. $\text{Cl}_6\text{C}_6\text{H}_6\text{O}_4\text{Sn}$. Calcd: C, 15.22; H, 1.27; O, 13.52; Cl, 44.93%.] M.P. 191-192°C (Gallenkamp apparatus, sealed capillary). Lit. 190-191°C (68). Molecular weight [440, 11.699 mg/ml CH_2Br_2 ; Theory, 473.5].

The mother liquor was again reduced in volume by 1/2 by rotary evaporation and ether was added. The resultant solution was reduced to a small volume and the solid present removed by filtration. The precipitate was washed with petroleum ether and briefly air dried. M.P. 190-191°C. Litt. 190-191°C (68).

B. Trichloroacetic acid (1.56 g, 9.56 mmol) was added to dimethyldivinyltin (0.917 g, 4.78 mmol). Following a very vigorous exothermic reaction, the clear, light amber liquid solidified to a tan solid mass on cooling. The solid mass was extracted with dichloromethane, the solution filtered, petroleum ether added, and the solution cooled in a refrigerator. The white crystals, which were isolated by filtration, melted over the range 100-130°C; therefore, they were recrystallized from chloroform/pentane. The resultant crystals started melting at 133°C with bubbling. The material was definitely not the desired product. Therefore, it was subjected to NMR examination in CDCl_3 solution. A very large resonance was

observed at 8.68τ relative to an external TMS standard. Methyl-tin couplings were observed on either side of the signal $J=82.6$ cps. Three other resonances of small intensity were also observed at 8.77 , 8.85 and 1.65τ .

C. Extreme measures were taken to preclude moisture entering the reaction.

A very vigorous reaction occurred when dimethyldivinyltin (1.0 g, 4.9 mmol) was added to trichloroacetic acid (1.58 g, 9.7 mmol). The contents of the flask became a clear brown liquid and frothed briefly. The solid tan mass, which formed on cooling, was extracted with dichloromethane. The extract was filtered in an apparatus protected from moisture, petroleum ether was added to the filtrate, and the solution placed in a freezer. The white solid which had formed was filtered, washed with pentane, and again recrystallized from dichloromethane/petroleum ether. The final crystalline product was dried in a P_2O_5 protected glove bag. The sample for analysis was loaded into a glass ampoule in the glove bag and sealed. [Found: C, 15.19; H, 1.96; O, 12.68; Cl, 33.18. $Cl_6C_6H_6O_4Sn$. Calcd: C, 15.22; H, 1.96; O, 13.52; Cl, 44.93%.] Tetramethyl-1,3-bis-(trichloroacetoxy)distannoxane, $Cl_6C_8H_{12}O_5Sn_2$ requires C, 15.05; H, 1.88; O, 12.53; Cl, 33.33%.

D. Extreme measures were taken to preclude moisture entering the reaction. All equipment was thoroughly flamed under nitrogen prior to use. All reactions were conducted under a dry nitrogen atmosphere.

Dimethyldivinyltin (2 ml), diluted with dichloromethane (2 ml), was added dropwise to a solution of trichloroacetic acid (3.94 g) in

dichloromethane (8 ml). The reaction was stirred magnetically during addition and for about 15 minutes after addition was complete. White precipitate formed immediately on adding sodium-dried pentane. Filtration in an apparatus protected from moisture, recrystallization from dichloromethane/petroleum ether, and drying in a nitrogen-filled glove bag, protected with P_2O_5 , produced the desired product. [Found: C, 15.29; H, 1.49; O, 13.57; Cl, 45.10. $Cl_6C_6H_6O_4Sn$. Calcd: C, 15.20; H, 1.27; O, 13.52; Cl, 44.94.]

Dimethyltinbis(2-chloro-2-methyl propionate).

Dimethyldivinyltin (1.5 ml, ≈ 9.2 mmole) and 2-chloro-2-methylpropionic acid (2.265 g, 18.6 mmoles) were combined in a 50 ml flask fitted with a condenser, and topped with a $CaCl_2$ drying tube. No reaction was evident after stirring magnetically 1/2 hour. The reaction was heated with a water bath (initial temperature $77^\circ C$) and changed from clear to milky within 30 minutes. After stirring overnight the reaction was cooled to room temperature. The reaction flask, containing white crystalline solid, was attached to the high vacuum system through a sublimator and vacuum applied at room temperature for several hours. No sublimate was evident; therefore, the reaction flask was immersed in a $77^\circ C$ bath. A small amount of sublimate formed after several hours. The sublimator apparatus was transferred to the glove bag (P_2O_5 dried) and dichloromethane added to the reaction flask. A small amount of white solid did not dissolve. Therefore, the mixture was filtered in the glove bag and pentane added to the filtrate. The crystals which formed on cooling and evaporation of the solvent, were filtered and dried in the glove bag.

[Found: C, 30.54; H, 4.63; O, 16.17; Cl, 17.94. $\text{Cl}_2\text{C}_{10}\text{H}_{18}\text{O}_4\text{Sn}$.

Calcd: C, 30.64; H, 4.60; O, 16.34; Cl, 18.10%.] Molecular weight

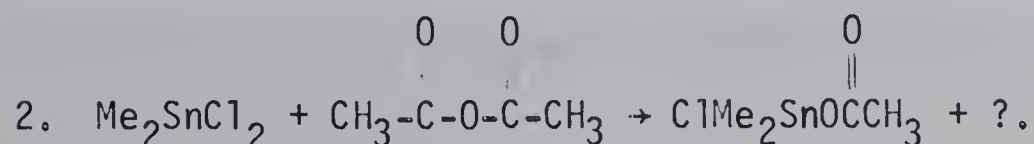
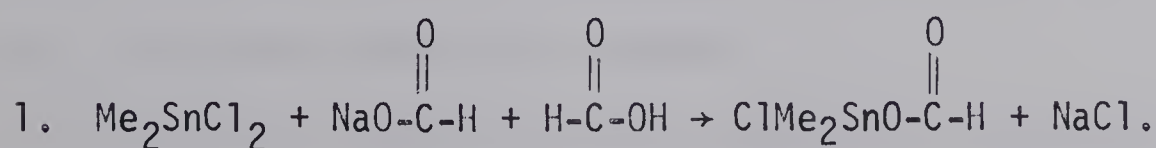
[455, 15.655 mg/ml CH_2Br_2 ; 476, 14.855 mg/ml CH_2Br_2].

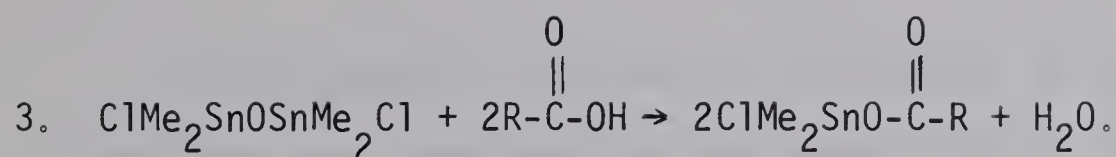
CHAPTER IV

DIMETHYLCHLOROTIN CARBOXYLATES

Dialkylchlorotin carboxylates in general, and dimethylchlorotin-carboxylates in particular, have not been extensively investigated. Okawara and Rochow (54) reported that dimethylchlorotin formate and dimethylchlorotin acetate were insoluble and therefore restricted their investigation to solid state infrared studies. The presence of a single Sn-C stretching vibration, and the similarity of $\text{-CO}_2\text{-}$ stretching vibrations to those observed in the sodium carboxylate salts, were interpreted on the basis of a linear C-Sn-C cationic skeleton and carboxylate anions. More recent studies of diethyl-, dipropyl- and di-n-butyl- chlorotin formate and acetate (10) have led to the suggestion that the acetates, which appear to be essentially monomeric in benzene, contain a chelating carboxyl group, a linear C-Sn-C skeleton, and five-coordinate tin. The formates were found to exist as monohydrates which decomposed in the course of sublimation giving a solid of broad melting range. Solid state infrared studies were interpreted as indicative of "formoxy groups of the ionic type" (13). It was assumed that a hexacoordinated tin atom was involved in the monohydrated formates.

Dimethylchlorotin carboxylates have been prepared by three different synthetic routes.





Reportedly the only carboxylate products isolated from these reactions were the desired dimethylchlorotin carboxylates.

The scarcity of experimental detail would seem to indicate straightforward reactions; however, during the course of this investigation the complexity of reactions 1 and 3 has been appreciated although not fully understood. Reaction of dimethyltin dichloride and the sodium salts of formic, isobutyric and pivalic acids resulted in a most unusual material believed to be a mixed trinuclear dimethyltin carboxylate species, (vide infra). Sodium dichloroacetate and dimethyltin dichloride in a 2:1 ratio yielded dimethylchlorotin dichloroacetate rather than dimethyltin bis(dichloroacetate).

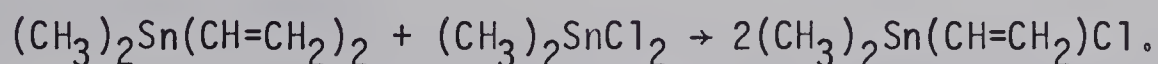
In spite of its apparent simplicity, reaction scheme 3 did not yield the desired product, because of the difficulty in obtaining pure tetramethyl-1,3-dichlorodistannoxane starting material. Repetition of the reported procedure (72) failed to produce the desired starting material. The distannoxane is reported to be insoluble and non-melting, therefore the only means of identification, short of x-ray crystallographic examination, is elemental analysis or identification of subsequent reaction products and deduction from the products as to the identity of the starting material. The material obtained in this study was appreciably deficient in both chlorine and oxygen. Reaction with formic acid resulted in the isolation of the unusual mixed trinuclear dimethyltin species.

Ultimately, dimethylchlorotin formate was obtained via cleavage of the vinyl group from dimethylvinyltin chloride.

A new procedure, believed to be superior to that given in the literature, was developed for the preparation of dimethylvinyltin chloride. Seyferth (73) prepared dimethylvinyltin chloride by cleaving one vinyl group from dimethyldivinyltin with hydrogen chloride.



Although the desired product is obtained by this procedure, one of the vinyl groups is lost as ethylene. Considerable effort is required to prepare dimethyldivinyltin, therefore more effective use of the vinyl groups on tin would greatly increase the overall efficiency of preparation. The following alternative route to dimethyl vinyltin chloride is believed to be more efficient and the ultimate in simplicity. Dimethyltin dichloride and dimethyldivinyltin in chloroform solution undergo a redistribution reaction when stirred together at room temperature. The desired dimethylvinyltin chloride is formed in about 90-95% yield as indicated by gas chromatographic measurement.



Purification by vacuum distillation was not successful. The ease of further redistribution was subsequently conclusively proved as attempted preparative gas chromatography resulted in the isolation of methyldivinyltin chloride, and trimethyltin chloride as well as dimethylvinyltin chloride in very poor yield. The identity of the products was established by NMR examination. Although it has not been demonstrated experimentally, it is suggested that removing the chloroform and unreacted dimethyltin dichloride by means of vacuum at a low temperature should result in isolation of the product in a reasonably

pure state, as dimethylvinyltin chloride is a liquid of fairly high boiling point (73-75°C @ 27 mm)(73).

Dimethylchlorotin-formate, -acetate and -dichloroacetate will be discussed together in view of the similarity in structural type. Following this discussion the rather unusual substances mentioned previously will be discussed.

RESULTS AND DISCUSSION

Dimethylchlorotin formate, Dimethylchlorotin acetate and Dimethylchlorotin dichloroacetate.

Dimethylchlorotin formate and dimethylchlorotin dichloroacetate were sufficiently soluble as prepared to allow the use of solution spectroscopy. Dimethylchlorotin acetate as prepared was not tested for solubility, but treated at 140°C in a sealed tube with cyclohexane to yield soluble crystals which were further purified by sublimation.

Molecular Weight Studies.

Dimethylchlorotin dichloroacetate and dimethylchlorotin acetate are not monomeric in methylene bromide solution. The degree of association observed in the acetate (2.41) appears to rule out a chelated monomeric species. The association indicated in the acetate apparently indicates that a large number of species may be present but that the weighted average may be approximated as a mixture of dimeric/trimeric species. No molecular weight studies were conducted with dimethylchlorotin formate.

Infrared Spectra.

Complete infrared data are given in Tables XXXIV, XXXV and XXXVI for the formate, acetate and dichloroacetate respectively.

Carbonyl-Carboxyl Region.

Examination of the tables clearly indicates some type of bridging $\text{-CO}_2\text{-}$ species exists in each of the compounds in chloroform solution. The strongest asymmetric $\text{-CO}_2\text{-}$ stretching frequency observed in the formate (1582 cm^{-1}) is nearly identical to that observed in polymeric and presumably cyclic trimethyltin formate (1580 cm^{-1}), and is therefore assigned to either a symmetrically bridged or symmetrically chelated formate group. The weaker 1620 cm^{-1} band is assumed to be due to the asymmetric stretching mode of a long-bonded formate group, and the 1650 cm^{-1} shoulder to arise from a free, ester-like formate group.

Dimethylchlorotin acetate exhibits a single strong asymmetric $\text{-CO}_2\text{-}$ stretching vibration at 1600 cm^{-1} . Again, a long-bonded acetate group is believed to account for the rather unusual frequency. In contrast, dimethylchlorotin dichloroacetate exhibits a shoulder at 1655 cm^{-1} and two strong asymmetric $\text{-CO}_2\text{-}$ absorptions at 1640 and 1615 cm^{-1} . The appearance of a doublet and the frequency separation are similar to observations made with trimethyltin dichloroacetate. Normal ester-type geometry may safely be dismissed as the observed frequencies are approximately 70 cm^{-1} lower than any previously reported for non-associated, ester-like dichloroacetate groups (43, 44). Indeed they are quite similar to frequencies previously assigned, in two different publications, to associated dichloroacetate groups (43, 45). In the latter paper, it was suggested that conformational

TABLE XXXIV

INFRARED SPECTRA FOR DIMETHYLCHLOROTIN FORMATE.

CHCl ₃	Nujol
1650 <u>sh</u>	1658 w-m
1620 w-m	1620 m-s
1582 s	1580 vs
1395 w	
1358 m	
	1315 s
	1205 w
	1193 w
1052 m-s	
873 m	
	815 m-s
	808 m-s
	782 s
610 s	615 m
	590 w-m
570 m	570 m
555 m	
520 w	520 w

TABLE XXXV

INFRARED SPECTRA FOR DIMETHYLCHLOROTIN ACETATE.

KBr	CHCl ₃	Nujol
	1760 w	
	1715 w-m	
	1600 s	
		1562 s
1550 s, br		
1450 m		
	1440 w-m	
1432 m		
	1420 w-m	
1405 m		1412 w
	1382 s	1385 m
	1335 s	1325 vw
	1290 w	
1208 w-m	1218 w	1215 w
1193 w		
	1050 w, br	
1012 w-m	1010 w	1018 w-m
943 w	942 w	953 vw
	915 vw	
		840 <u>sh</u>
		812 <u>sh</u>
790 m-s		797 m
		767 w
		725 w
678 s		687 s
	618 w-m	615 w
608 w-m		
576 w-m	568 w-m	575 w-m
	562 <u>sh</u>	
528 w-m	528 w	526 w
492 w-m		493 w
		425 w, br

TABLE XXXVI

INFRARED SPECTRA FOR DIMETHYLCHLOROTIN DICHLOROACETATE.

KBr	CHCl ₃
2995	
2925	
	1770 sh
	1755 sh
	1745 m
	1735 m
1665 m	1655 sh
1635 <u>sh</u>	1640 s
1622 <u>s</u>	1615 s
1390 <u>sh</u>	1390 m
1368 <u>sh</u>	
1362 m-s	1362 s
1298 <u>sh</u>	
1245 <u>sh</u>	
1233 m-s	
1220 sh	
1203 w	
1195 w-m	
1190 <u>sh</u>	
	1068 w
942 w	948 w
937 w	
818 m	
795 s	
780 <u>sh</u>	
732 m-s	
712 m	
575 w	580 w
560 vw	565 w-m
	550 <u>sh</u>
	540 <u>sh</u>
518 vw	518 <u>sh</u>
	512 <u>sh</u>
	505 w-m
495 w	
468 w	

effects (see Chapters II and III) would not be expected in symmetrically bridged chloroacetate derivatives; however, such effects could still be operative in long-bonded dichloroacetate groups, and indeed it is considered that the observation of two strong absorptions supports the long-bonded hypothesis.

Solid state studies indicate that symmetrical bridging or symmetrical chelation predominates in the formate, and occurs exclusively in the acetate; asymmetric absorptions are observed at 1658, 1620 and 1580 cm^{-1} in the formate and at 1562 cm^{-1} in the acetate. The three absorptions observed in the formate are believed to be due to ester-like (1658 cm^{-1}) long-bonded (1620 cm^{-1}) and symmetrically bridged (1580 cm^{-1}) formate groups. Clearly, the 1580 cm^{-1} absorption may also be due to a symmetrically chelated formate group.

Dimethylchlorotindichloroacetate spectra contain a medium absorption at 1665 cm^{-1} , a shoulder at 1635 cm^{-1} and a strong peak at 1622 cm^{-1} . All three of these absorptions are within the region normally associated with an asymmetric $-\text{CO}_2-$ stretching mode of a chelated or associated dichloroacetate group. The presence of more than one absorption could conceivably be due to the presence of long-bonded dichloroacetate groups in more than one configuration in the solid state.

Tin-Carbon Stretching Region.

Non-linear C-Sn-C geometry appears to be indicated for all three compounds in chloroform solution. Dimethylchlorotin formate and dimethylchlorotin acetate spectra contain absorptions at 570 and 568 cm^{-1} respectively, assignable to the asymmetric Sn-C₂ stretching mode. Weak absorptions at 520 and 528 cm^{-1} are believed to be due to

the symmetric Sn-C_2 stretching mode of the formate and acetate respectively. The additional band at 555 cm^{-1} observed in the formate is somewhat puzzling. The frequency is very similar to that observed in trimethyltin carboxylates and assigned to the asymmetric Sn-C_3 stretching mode. It is possible that a redistribution reaction occurred during preparation with trimethyltin formate as a reaction product. The very close agreement between theory and experimental results on elemental analysis rules out the presence of all but a very small concentration of trimethyltin formate.

The dimethylchlorotin dichloroacetate spectrum shows definite bands at 580 and 565 cm^{-1} as well as shoulders at 550 , 540 , 518 and 512 cm^{-1} . The 565 and 518 cm^{-1} absorptions are assigned respectively to asymmetric and symmetric Sn-C_2 stretching modes. It is possible that the 550 and 512 cm^{-1} shoulders arise from a small concentration of trimethyltin dichloroacetate, but again, the elemental analysis rules out all but a very small concentration of this impurity. The origin of the 500 cm^{-1} peak and the 540 cm^{-1} shoulder is unknown.

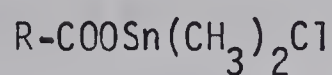
The non-linear Sn-C_2 skeleton observed in chloroform appears to exist in the solid state as well. Each spectrum contains absorptions in the $570\text{-}576\text{ cm}^{-1}$ and $518\text{-}528\text{ cm}^{-1}$ region. Significantly, the 555 cm^{-1} absorption observed in the chloroform solution spectrum of the formate and the 550 , 540 and 512 cm^{-1} shoulders observed in the dichloroacetate are absent. Absence of the absorptions near 550 cm^{-1} casts doubt on the presence of a trimethyltin species.

NMR Spectra.

NMR parameters of dimethylchlorotin-formate, -acetate, and -dichloroacetate are listed in Table XXXVII. The higher chemical

TABLE XXXVII

PROTON MAGNETIC PARAMETERS FOR DIMETHYLCHLOROTIN CARBOXYLATES.



R	Solvent	Temp. °C	$\text{CH}_3\text{-}\overset{\text{Sn}}{\underset{ }{\text{C}}}$	J^1 cps	J^2 cps	R τ
H	CDCl_3	R.T.	8.80	74.3	71.3	1.62 (a)
CH_3	CDCl_3	R.T.	8.82	72	70	7.78 (b)
CH_3	CDCl_3	R.T.	8.89	74.5	71.3	(c)
Cl_2HC	CDCl_3	55	9.07	70.4	67.2	(d)
	CDCl_3	25	9.08	70.5	67.4	(d)
	CDCl_3	0	9.11	70.1	66.9	(d)
	CDCl_3	-10	9.12	70.0	67.1	(d)
	CDCl_3	-30	9.12	70.6	67.4	(d)

(a) External TMS reference, A-60 spectrometer.

(b) Internal TMS reference, A-60 spectrometer.

(c) HA-100 spectrometer, TMS reference.

(d) HA-100 spectrometer, benzene reference, masked methine resonance.

shift value observed in the dichloroacetate for the methyl protons on tin is believed to result from the use of benzene as solvent.

The greater magnitude of the spin-spin couplings in the formate and acetate ($J \approx 74$ cps) in relation to the dichloroacetate ($J \approx 70$ cps) is in generally good agreement with the molecular weight data. The degree of association observed in the acetate (2.4) and the predominance of long-bonded $\text{-CO}_2\text{-}$ vibrations in its infrared spectrum are consistent with a long-bonded associated species. The magnitude of the couplings is less than that observed for chelated dimethylchlorotin oxinate ($J \approx 77$ cps) (53). As was pointed out in the previous chapter the significance of the coordination state of the tin atom must be considered a matter for further study; thus the presence of presumably 5-coordinate tin in the oxinate is considered to be of questionable significance. The changes in geometry of the Sn-C_2 skeleton on chelation however are of paramount importance. A non-chelated, non-bridged dimethylchlorotin molecule would presumably have essentially tetrahedral geometry around the tin atom. Chelation or bridging would necessitate a change in geometry and it is reasonable to assume that the more symmetrical the chelated ligand-tin bonds, the greater the change in geometry. If the carboxylate groups were chelated or symmetrically bridged, one might expect that the magnitude of J should be roughly comparable to that observed in dimethylchlorotin oxinate (77 cps) (53). The observed magnitude of J (≈ 74 cps), is slightly greater than that observed in presumably tetrahedral dimethyltin dichloride (71 cps). It is reasonable to assume that the C-Sn-C bond angle is slightly greater than the tetrahedral angle. If the conditions set down in Chapter III for predicting the

C-Sn-C bond angle are applicable in these compounds as well, it is suggested that the formate and acetate C-Sn-C bond angle is about 118° .

Dimethylchlorotin dichloroacetate is believed to exist as a tetrahedral molecule in chloroform solution. The essentially identical magnitude of J (≈ 70 cps) to that of dimethyltin dichloride (71 cps), and lack of change in the magnitude of J over a temperature range of 85° , support a near-tetrahedral carbon-tin-carbon angle.

The increase in the chemical shift of the methyl groups on tin with decreasing temperature implies a varying degree of association equilibrium in the system. Such an equilibrium may be classed as either intramolecular long-bonded chelated or intermolecular long-bonded bridged. Both systems are considered possible and little preference can be attached to either proposal at this time. The following factors reflect the changes taking place within the system.

1. The constancy of J indicates a minimal change in geometry about tin or of the dimethyltin group in particular.

2. Two strong asymmetric $\text{-CO}_2\text{-}$ stretching vibrations observed in the infrared spectrum implies a dissymmetric dichloroacetate group.

3. The very limited molecular weight data suggest some type of intermolecular association rather than intramolecular association but much more extensive molecular weight studies must be conducted before a definite choice can be made.

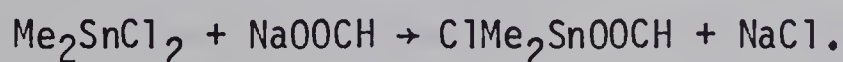
Unusual Reaction Products.

As mentioned earlier in this chapter unusual products were

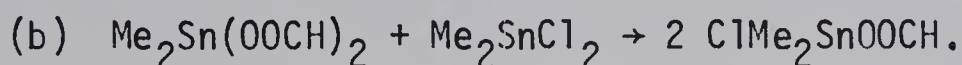
isolated from reactions involving dimethyltin dichloride and the sodium salts of formic, isobutyric and pivalic acid. These reactions are now discussed. The experimental evidence presented, and possible structures postulated.

Presumably the reacting species involved in reaction (1) are dimethyltin dichloride and the sodium salt of the carboxylic acid involved. It has been presumed that the direction of the reaction may be controlled by the molar ratio of the reacting species. Previous workers have stated that the use of less than an equimolar amount of carboxylate salt results in the preparation of the desired dimethylchlorotin carboxylate (54). The mechanism of this type of reaction is unknown and it is not clear how the final product is formed. At least two reaction paths are possible.

1. The product forms directly.



2. The product of step (1) undergoes further reactions.



Previous publications (54) have reported dimethylchlorotin carboxylates as the only product isolated; however, a roughly analogous reaction between dimethyltin dichloride and the sodium salt of manganese pentacarbonyl in a 1:1 mole ratio resulted in dimethylchlorotin manganese pentacarbonyl or dimethyltinbis(manganese pentacarbonyl), depending on the rate of addition of the dimethyltin dichloride to the sodium salt solution and the isolation procedure used (74). If the addition was rapid and the product was isolated immediately, dimethyltin bis(manganese pentacarbonyl) was obtained.

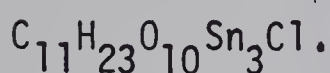
Dimethylchlorotin manganese pentacarbonyl was obtained with slow addition and overnight cooling in a refrigerator prior to isolation. Speculation as to possible reaction paths analogous to (2a) and (2b) is reasonable.

Complex formation via association is well established in organotin carboxylate chemistry, therefore it is not unreasonable to postulate the formation of a complex via carboxylate bridging between the products of reaction steps (1) or (2b), and (2a) in varying proportions.

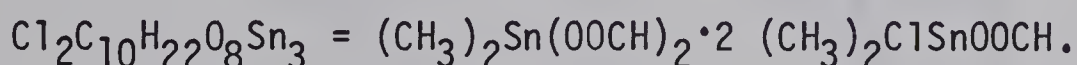
Tetramethyl-1,3-dichlorodistannoxane reportedly (10) yields the corresponding dimethylchlorotin carboxylate in quantitative yield when treated with a carboxylic acid. The key factor involved in these reactions is the preparation of the distannoxane. Recent publications (14, 75, 76) have made it abundantly clear that the preparation of dichlorodistannoxanes may yield several products depending on the experimental procedures used. Difficulties in obtaining pure tetramethyl-1,3-dichlorodistannoxane by the method of Okawara and Wada (72) are believed to be due to the lack of detailed experimental procedures. The possibility of forming tristannoxanes, tetrastannoxanes, 1-chloro-3-hydroxy tetramethyldistannoxanes, etc., in these preparations cannot be ruled out.

The reaction product obtained by reaction routes (1) and (3) will now be discussed. Elemental analysis of the white solid sublimate obtained from the reaction of dimethyltin dichloride (0.0137 mole), sodium formate (0.0109 mole) and excess formic acid indicated a simplest empirical formula of $C_{10}H_{22}O_8Sn_3Cl_2$. Similarly, the white, solid sublimate obtained from the reaction of presumed

tetramethyl-1,3-dichlorodistannoxane (prepared according to Okawara and Wada (vide supra) but not analyzing satisfactorily for this compound) and formic acid was analyzed and found to correspond to exactly the same empirical formula. The product from the distannoxane reaction, after heating overnight at 140°C in a sealed tube with cyclohexane, formed beautiful long needles on cooling, which still had the empirical formula $C_{10}H_{22}O_8Sn_3Cl_2$. Surprisingly, the material obtained by the same reaction route in a different preparation, after treatment with cyclohexane at $\approx 100^\circ C$ overnight followed by two days at 140°C, corresponded to an empirical formula approaching



	C	H	O	Cl	Sn
Found, %	17.24	3.33	18.33	9.84	51.26
Atomic Ratio	1.437	3.33	1.145	0.277	0.432
Equivalent to	10.37	24.0	8.271	2	3.12
Calcd. for $Cl_2C_{10}H_{22}O_8Sn_3$	17.21	3.15	18.36	10.17	51.11



Infrared Spectra.

Infrared examination of these materials revealed two strong asymmetric $-CO_2-$ absorptions in the 1615-1575 cm^{-1} region in chloroform solution (Figure 27) but only one strong absorption in the 1560-1570 cm^{-1} region in the solid state (Figure 28). Assignment of the 1560-1570 cm^{-1} band to a symmetrically bridged formate group seems certain in view of previous observations on trimethyltin formate. The 1615-1575 cm^{-1} absorption is tentatively assigned to a long-bonded formate group. It is apparent from the frequency of the

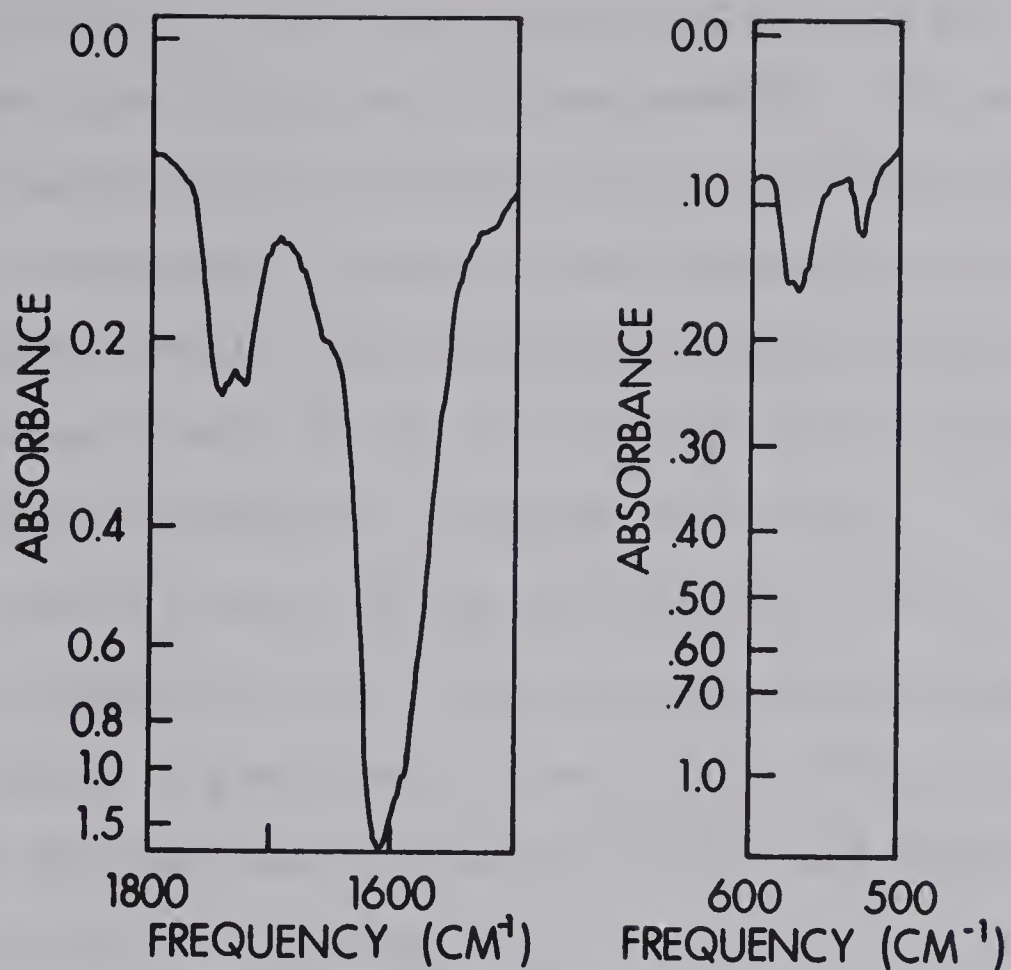
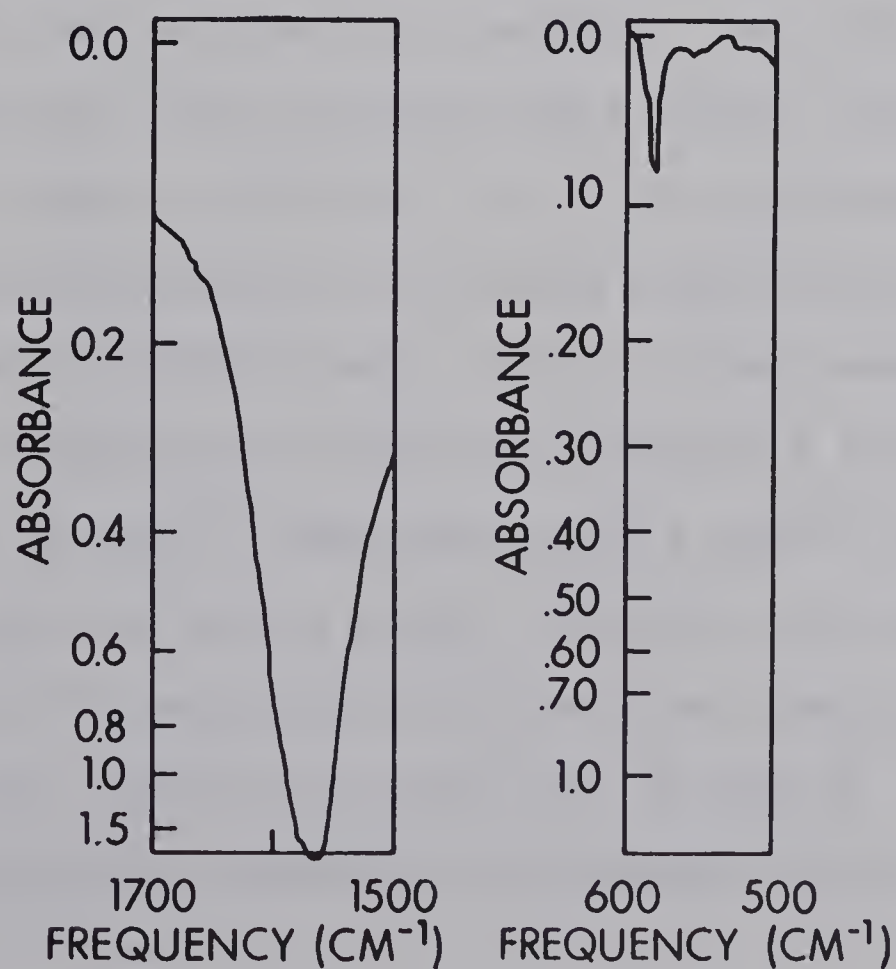


Figure 27. Infrared spectra for trinuclear methyltin formate in chloroform.

Figure 28. Infrared spectra for trinuclear methyltin formate, nujol mull.



-CO₂- absorptions in solution and in the solid state, that association of some type is operative in these materials. The empirical formula is suggestive of a trinuclear associated formate species composed of two molecules of dimethylchlorotin formate and one molecule of dimethyltin diformate. Unfortunately, infrared studies of the carbonyl-carboxyl region do not seem to allow differentiation between the two different carboxylates presumed to be present. Tin-carbon stretching region studies indicate that the Sn-C₂ portion of the molecules are most likely non-linear in solution, and perhaps also in the solid state, as absorptions in the 580-560 cm⁻¹ and 530-510 cm⁻¹ region are observed clearly in solution spectra and somewhat ambiguously in solid state spectra.

NMR Studies.

NMR studies offered the greatest potential for resolving the problem of the composition of the unusual materials. Unfortunately, the expectations were only partially realized. Two strong sharp resonances are observed in CDCl₃ solution (Table XXXVIII, Figure 29). The strongest resonance (8.78-8.90 τ) is clearly due to methyl groups on tin, as spin-spin couplings are observed symmetrically disposed about the resonance (J=75-77 cps). The other strong resonance (1.58-1.69 τ) is assignable to the single proton of a formate group. Integration of the signal intensities reveals a ratio of approximately 4.5 methyl protons per formate proton. This ratio is in agreement with a 2:1 ratio of dimethylchlorotin formate and dimethyltin diformate which has a theoretical proton ratio of 4.5/1.0.

A single methyltin resonance is inconsistent with the two dif-

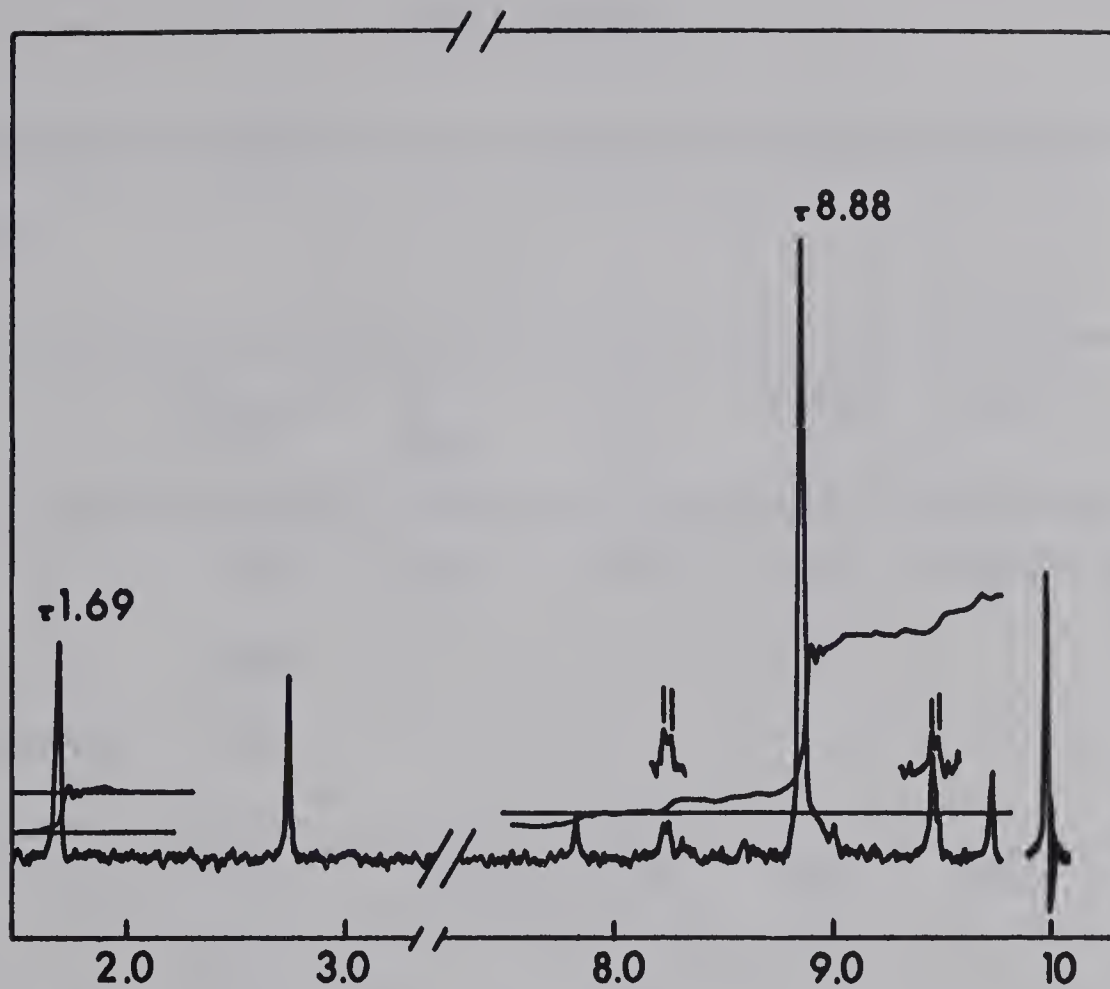


Figure 29. NMR spectra for trinuclear methyltin formate.

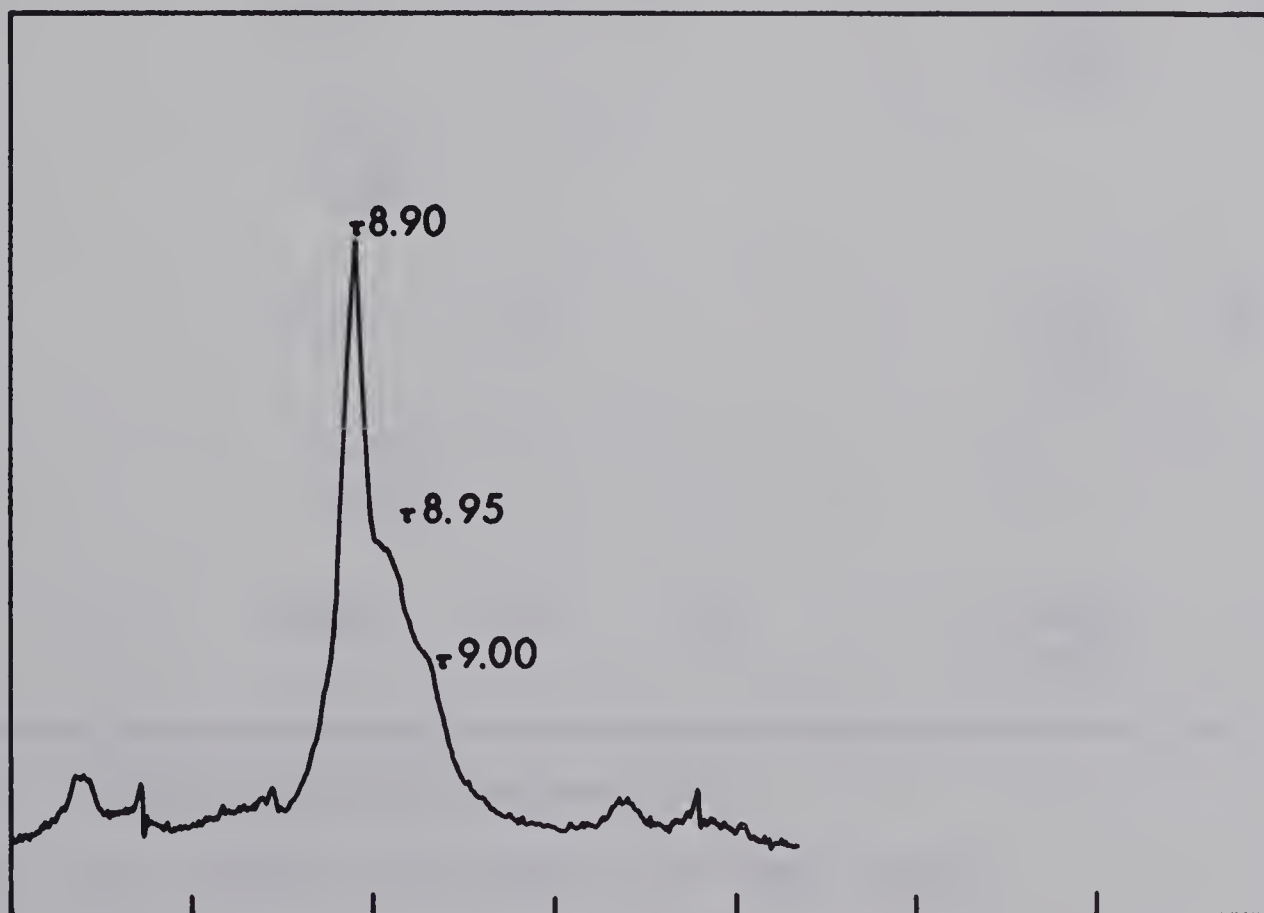


Figure 30. NMR (100 mHz) of methyltin region of trinuclear methyltin formate.

TABLE XXXVIII

PROTON MAGNETIC PARAMETERS FOR TRINUCLEAR METHYLTINCARBOXYLATE MATERIAL.

	$\text{CH}_3\text{-Sn}$ τ	J^1 cps	J^2 cps	H-COO τ	Solv.	Temp. °C
	8.88	75.4	71.4	1.69	CDCl_3	R.T. (a)
Ratio	4.56			1		
Theory Ratio	4.50			1		
	8.78	75.4	71.8	1.58	CDCl_3	R.T. (a)
Ratio	4.17			1		
Theory Ratio	4.50			1		
	8.90	≈ 77			CDCl_3 CHCl_3	33.5 (b)
	8.95 8.98					
	8.89	76			CDCl_3 CHCl_3	33.5 (c)
	8.93 8.98					
	8.88	79	76		CDCl_3 CHCl_3	0 (c)

(a) External TMS, A-60 spectrometer.

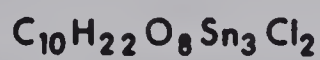
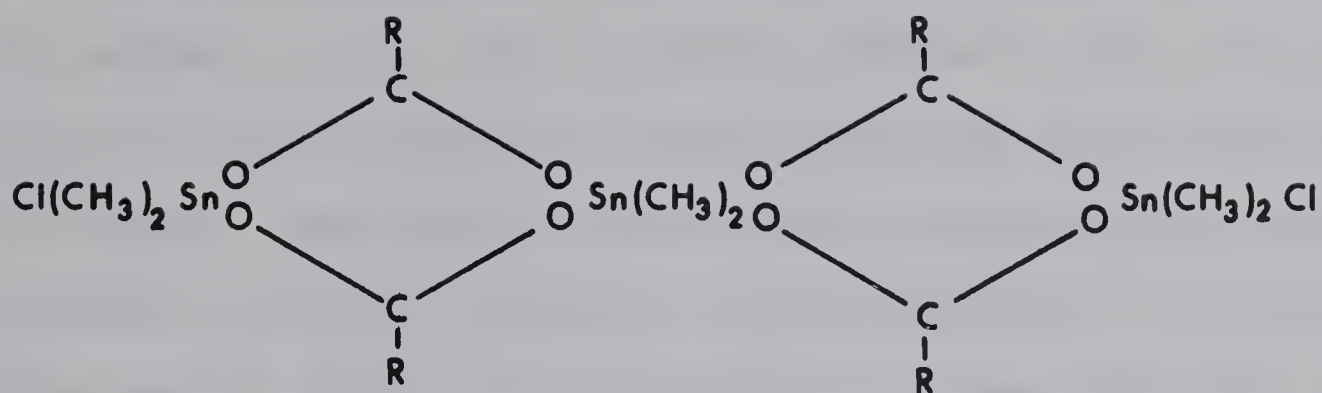
(b) CHCl_3 , HA-100 spectrometer, 250 sweep width.

(c) CHCl_3 , HA-100 spectrometer, 100 sweep width.

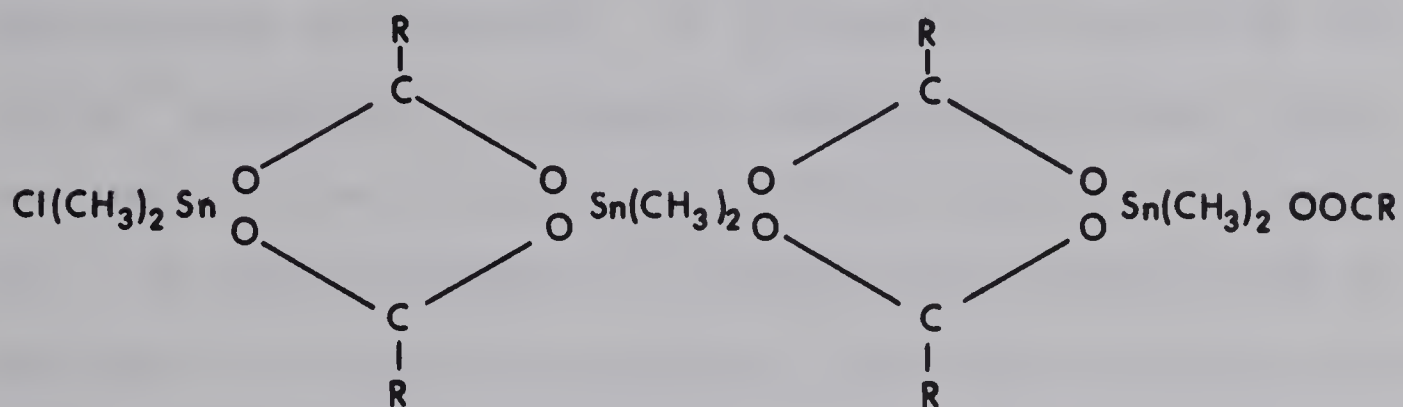
ferent types of molecules believed to be present, unless the chemical shift of methyl groups in each molecule are identical or some type of fast exchange is occurring in the system. Examination of the materials by 100MHz NMR indicates that the methyltin resonance observed as a single band at 60 mHz is indeed more complex (Figure 30). Two definite shoulders at 8.95 and 9.00 τ may be due to methyl groups on tin of the complex or they may be due to methyl groups on tin of impurity hydrolysis/condensation product tetramethyl-1,3-diformoxy-distannoxane.

Additional work and ultimately an x-ray investigation, will be necessary to establish definitively the structure of these materials. However, the temptation to indulge in some speculation as to these structures is irresistible, and accordingly, drawings XV, XVI and XVII are suggested. These require little comment except to note the polymeric aspect emphasized in XVII, where dimethyltindiformate constitutes the monomeric unit and dimethylchlorotinformate the end group.

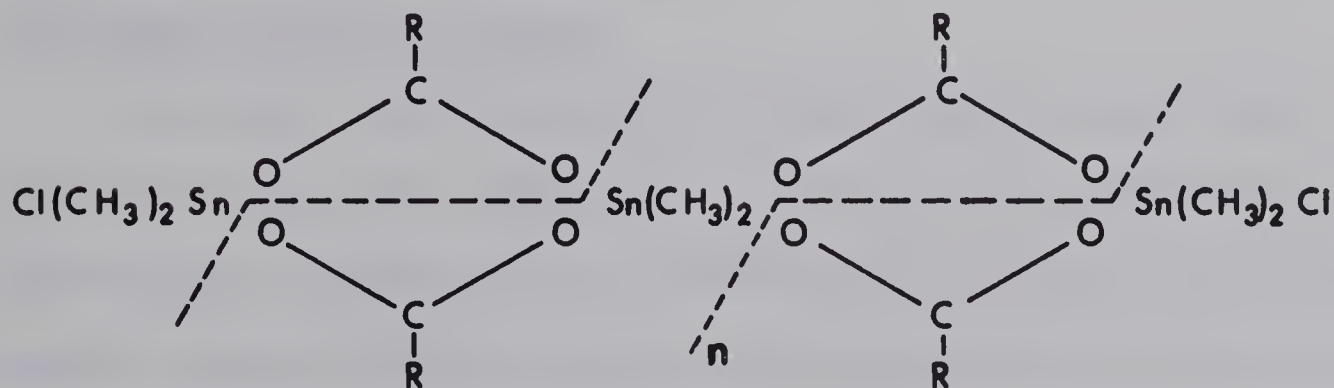
Analysis of the white solid sublimate obtained from the reaction of dimethyltindichloride and sodium isobutyrate in butyl ether resulted in very good carbon-hydrogen values for dimethylchlorotin isobutyrate but low oxygen and chlorine values. It would not be unreasonable to assume the material was mainly dimethylchlorotin-isobutyrate contaminated with small amounts of impurities. However, such an assumption appears to be unjustifiable in view of the evidence (vide infra).



XV



XVI



$n = 4$, DIMER OF ABOVE



XVII

Infrared Spectra.

Infrared examination of the material in solution (Figures 31 and 32) revealed a strong $\text{-CO}_2\text{-}$ absorption (1590 cm^{-1} , CHCl_3 ; 1596 cm^{-1} , C_6H_{12}) as well as shoulders or medium absorptions in the $1555\text{-}1565\text{ cm}^{-1}$ region. Additionally, the chloroform solution spectrum exhibited a shoulder (1606 cm^{-1}) preceeding the main absorption. The solid state spectrum (Figure 33) is essentially the same (1605 cm^{-1} , sh; 1583 cm^{-1} , strong; 1547 cm^{-1} , strong and broad). Complete infrared data are given in Table XXXIX. It is reasonable to assign the $1547\text{-}1565\text{ cm}^{-1}$ absorption to a presumably symmetrically bridged isobutyrate group in view of the frequency and the intensity of the absorption. The strong $1583\text{-}1596\text{ cm}^{-1}$ absorption and the weaker 1605 cm^{-1} absorption are tentatively assigned to long-bonded isobutyrate groups of an associated species.

Tin-Carbon Stretching Region.

Tin-carbon stretching region studies suggest a non-linear Sn-C_2 skeleton in the solid state and in solution, as the absorptions are observed near $560\text{-}580\text{ cm}^{-1}$ and $520\text{-}530\text{ cm}^{-1}$, regions of the spectrum normally associated with asymmetric and symmetric tin-carbon stretching modes respectively.

NMR Spectra.

Once again, the value of NMR examination of methyltin carboxylate compounds was demonstrated. Examination of the material in CDCl_3 solution (Table XL, Figure 34) suggested a trinuclear associated species was present. Methyltin resonance was observed at 8.88τ with the normal spin-spin coupling satellites ($J=77\text{ cps}$). A doublet

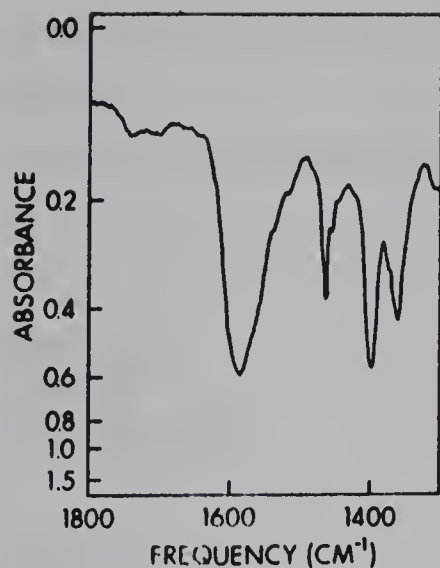


Figure 31.

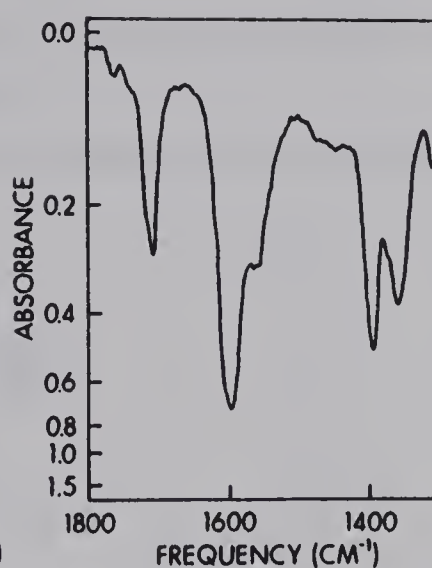
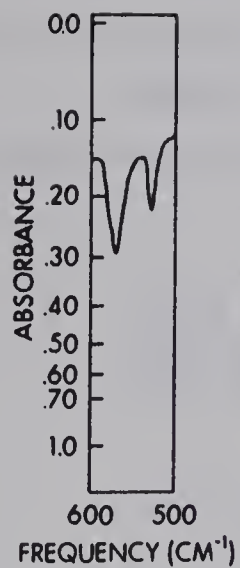


Figure 32

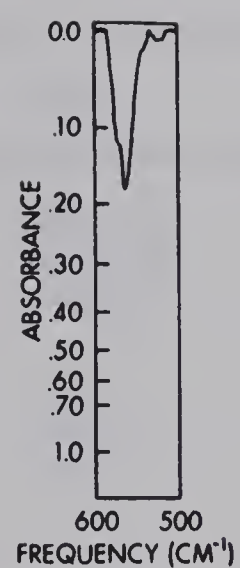


Figure 31. Infrared spectra for trinuclear methyltin isobutyrate in chloroform.

Figure 32. Infrared spectra for trinuclear methyltin isobutyrate in cyclohexane.

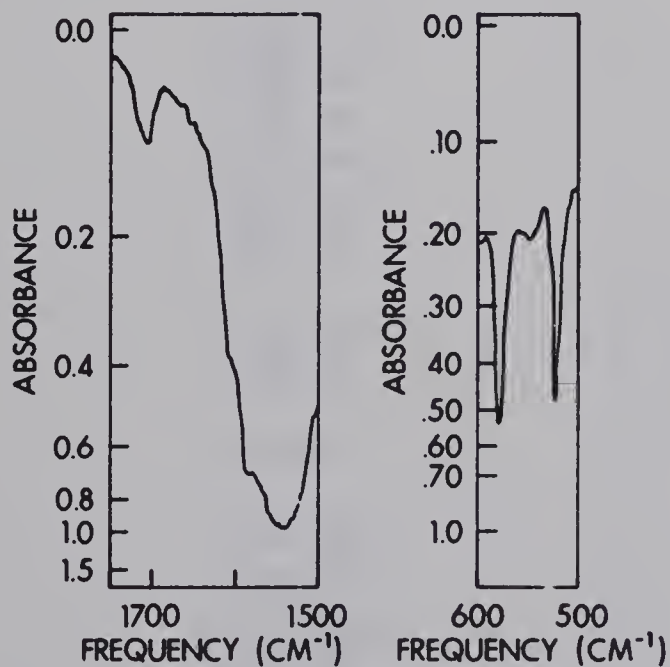


Figure 33. Infrared spectra for trinuclear methyltin isobutyrate, nujol mull.

TABLE XXXIX

INFRARED SPECTRUM FOR TRINUCLEAR METHYLTINISOBUTYRATE MATERIAL.

CHCl_3	Nujol	C_6H_{12}
		1760 vw
		1718 <u>sh</u>
	1702 w	1708 <u>m</u>
1606 <u>sh</u>	1605 <u>sh</u>	
1590 <u>s</u>	1583 <u>s</u>	1596 s
1565 <u>sh</u> , br		1565 m
	1547 s, br	1555 m
1470 m		
1460 w		
	1418 s	
1405 s		
		1393 m
1378 <u>sh</u>		
1365 <u>m-s</u>		1360 m
	1312 s	
	1293 m	1290 <u>sh</u>
1263 m-s	1265 m	1262 <u>sh</u>
		1250 <u>m</u>
	1205 vw	1200 vw
	1195 w	1195 vw
	1190 w	
	1165 w	1168 w
1100 w-m	1102 <u>sh</u>	1095 w-m
1086 w-m	1085 <u>s</u>	1080 w-m
		980 vw
	963 vw	
935 w	928 m	930 w-m
862 w		
	850 m	
820 w, br		835 <u>sh</u>
	792 <u>sh</u>	
	780 <u>s</u>	785 s
	760 <u>sh</u>	
	670 <u>s</u>	
	640 vw	
620 m		625 w-m
580 <u>sh</u>	570 m	570 <u>sh</u>
568 <u>m</u> , br		565 <u>m</u>
	550 vw	
530 w-m	524 m	525 vw

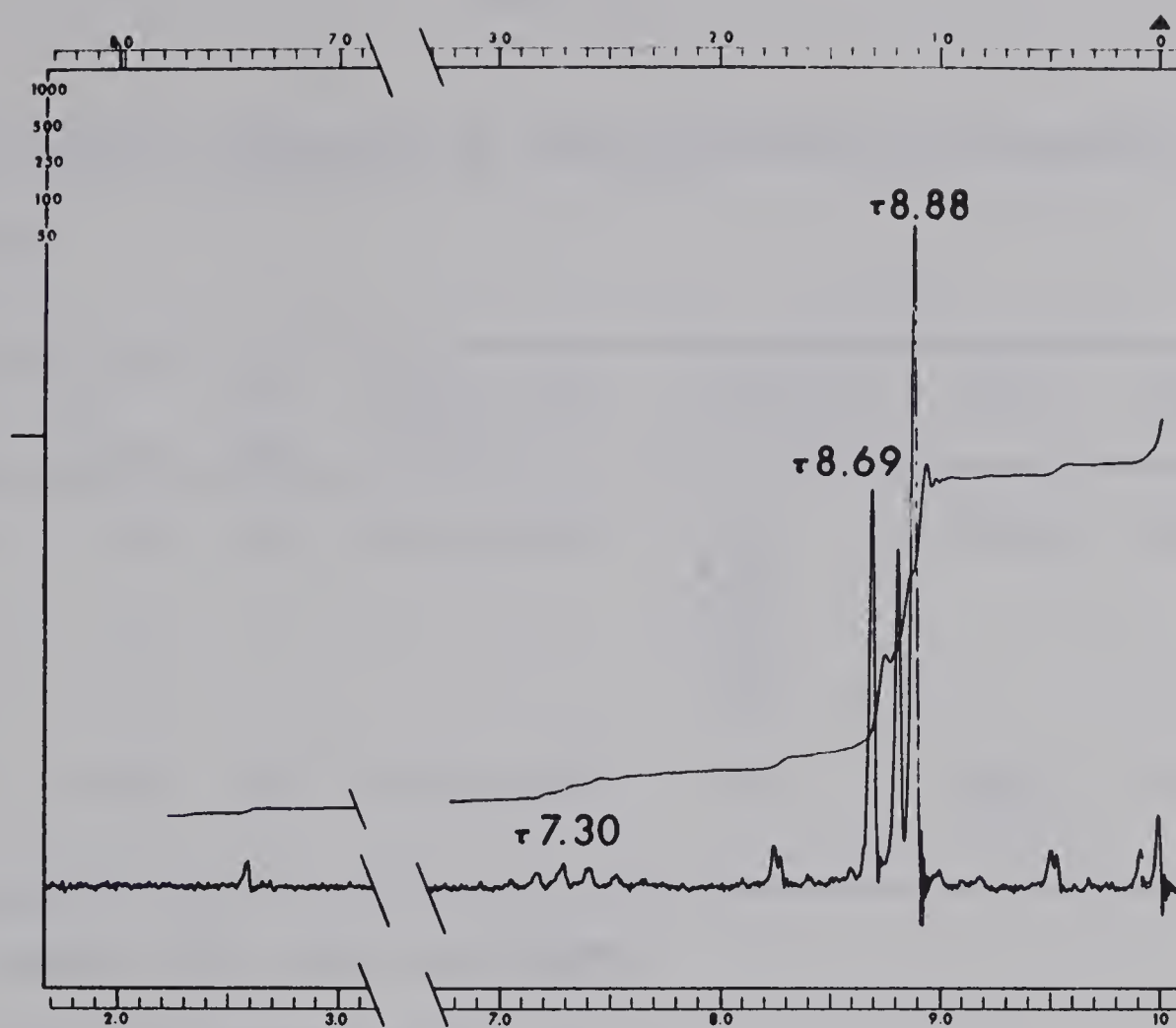


Figure 34. NMR spectra of trinuclear methyltin isobutyrate in CDCl_3 .

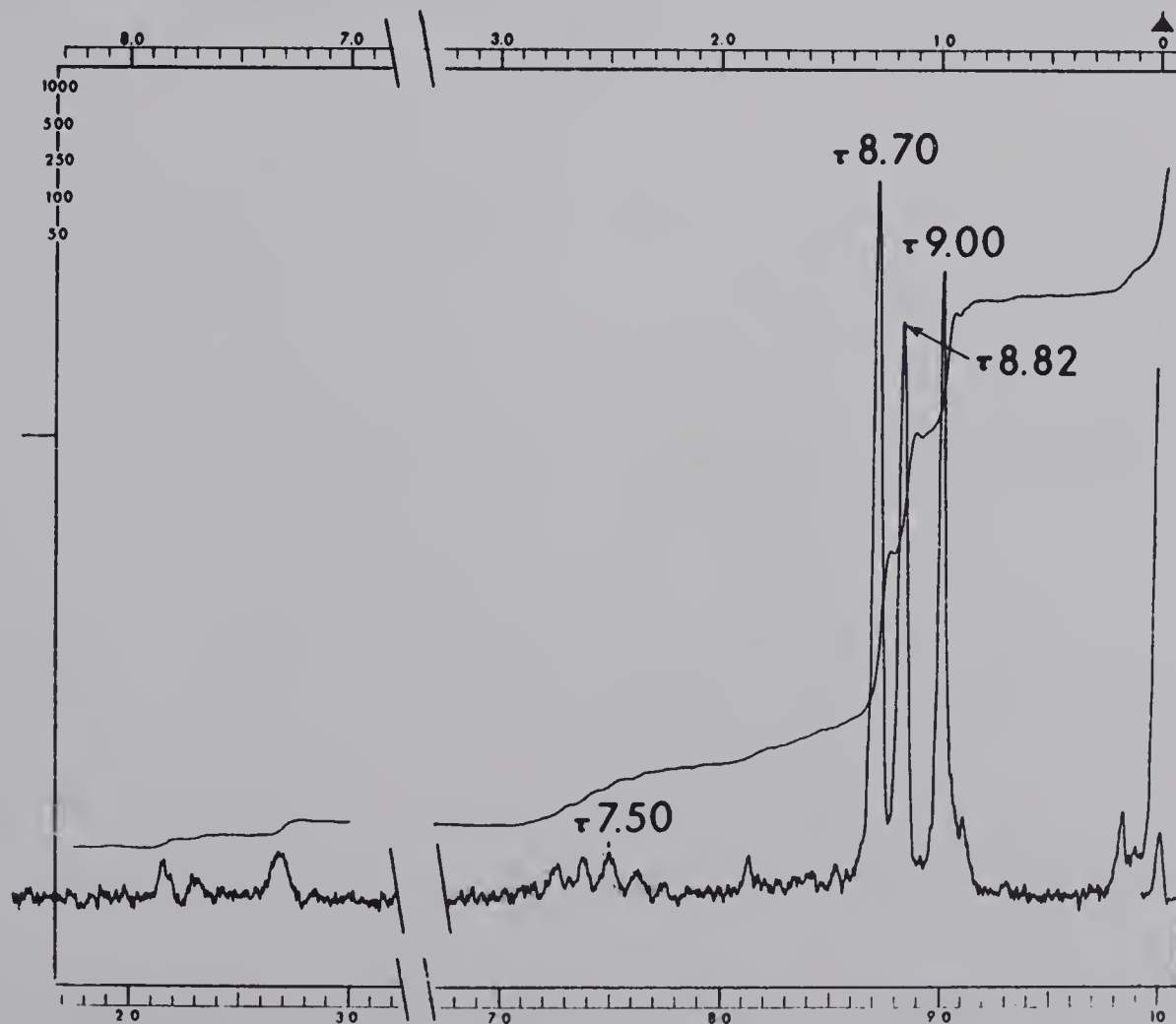


Figure 35. NMR spectra of trinuclear methyltin isobutyrate, pyridine-d_5 added.

TABLE XL

PROTON MAGNETIC PARAMETERS FOR TRINUCLEAR METHYLTIN ISOBUTYRATE
MATERIAL

$\text{CH}_3\text{-}\underset{\sim}{\text{Sn}}$	J^1 cps	J^2 cps	$\text{H}(\text{CH}_3)_2\text{-COO}$ $\underset{\sim}{\text{C}}$	$\text{H-}(\text{CH}_3)_2\text{C}$ $\underset{\sim}{\text{C}}$	Solv.	Temp.
8.88	77	74	8.81, 8.69	7.07 7.19 7.30 7.43 7.52	CDCl_3	R.T. (a)
9.00	106	102	8.82, 8.70	7.50	CDCl_3 (b)	R.T. (a)

(a) Internal TMS, A-60 spectrometer.

(b) Excess pyridine- d_5 added.

readily assignable to the six methyl protons of an isobutyrate group was observed at 8.81 and 8.69 τ . Five peaks of the expected septet for the methine proton were observed centered at 7.30 τ . Integration of the signal intensities provided the key to understanding the identity of the material. A trinuclear species composed of two molecules of dimethylchlorotin isobutyrate and one molecule of dimethyltin diisobutyrate would be expected to exhibit resonances in a ratio of 4.5 methyltin protons/6 isobutyrate methyl protons/1 isobutyrate methine proton. The experimentally observed ratio of 4.36/6/1 is in reasonably good agreement with theory. The magnitude of J suggests that the Sn-C₂ skeleton is non-linear and may be very similar to that of dimethylchlorotin oxinate (77.6 cps) (53) which has been discussed previously in this thesis and suggested (53) as possessing five-coordinate tin with a chelating oxinate group. The change in the magnitude of J on adding an excess of pyridine-d₅ (J=106 cps) tends to confirm the non-linearity of the Sn-C₂ skeleton (Figure 35).

Inadvertently, no elemental analysis was obtained on the sublimed product resulting from the reaction of dimethyltin dichloride (0.05 mole) and sodium pivalate (0.05 mole) in refluxing butyl ether. The identity of the material was established based on interpretation of infrared and NMR spectroscopic results (Table XLI).

Strong absorptions are observed at 1595 and 1563 cm⁻¹ in the chloroform solution spectrum (Figure 36). In addition, weak absorptions and shoulders are observed at 1695, 1572, 1540 and 1520 cm⁻¹. It is reasonably safe to assign the 1563 cm⁻¹ band to a symmetrically bridged or chelated pivalate group. The 1595 cm⁻¹ absorption may be due to a long-bonded bridging or chelating pivalate group. The over-

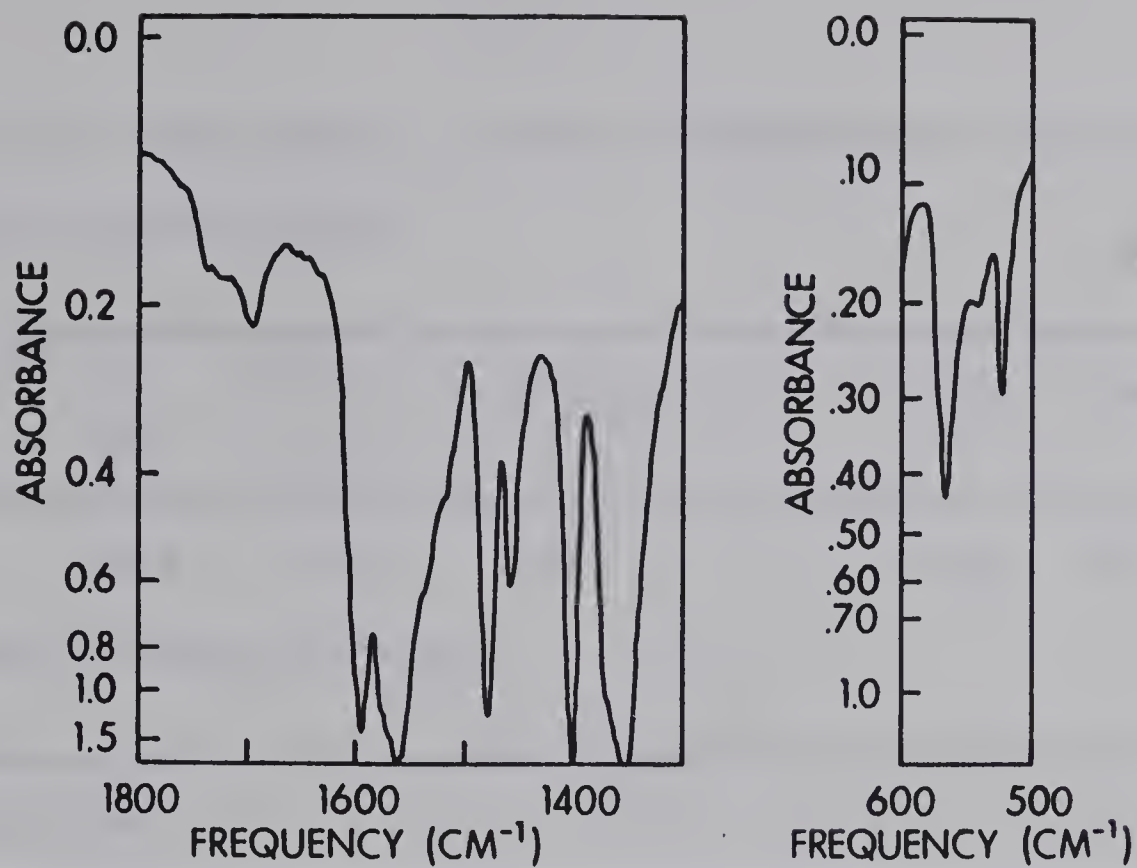


Figure 36. Infrared spectra for trinuclear methyltin pivalate in chloroform.

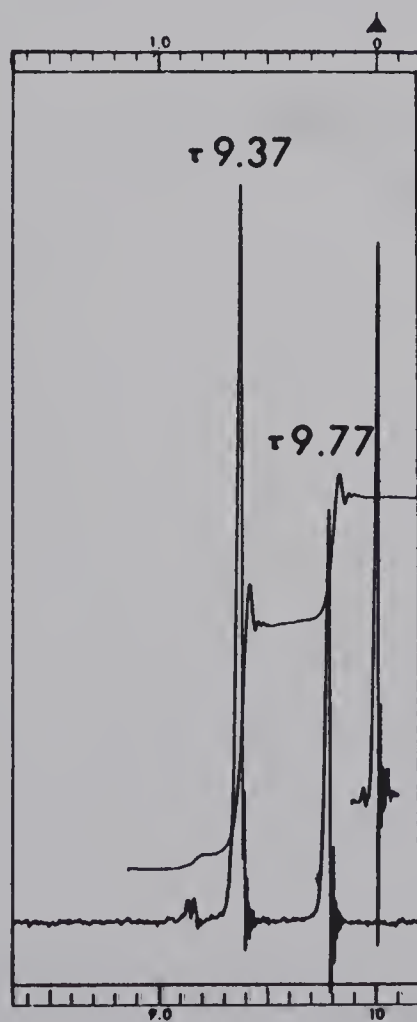


Figure 37. NMR spectra of trinuclear methyltin pivalate in benzene.

TABLE XLI

INFRARED AND PROTON MAGNETIC RESONANCE PARAMETERS FOR TRINUCLEAR
METHYLTIN PIVALATE MATERIAL

$\text{CH}_3\text{-Sn}$ τ	J^1 cps	J^2 cps	$(\text{CH}_3)_2\text{C-COO}$ τ	Solv.	Temp.
9.77	76.9	73.5	9.37	C_6H_6	R.T. (a)

ppt forms on adding pyridine- d_5

CHCl_3 , Infrared

1730 sh, br
1695 w
1595 s
1572 sh
1563 vs
1540 sh
1520 sh
1478 s
1458 m
1400 s
1370 sh
1355 vs
1122 vw
1095 vw
1020 w
938 w
908 m
855 w, br
815 w, br
625 m
618 m
566 m
541 w
523 w-m
430 w-m

(a) External TMS, A-60 spectrometer.

all geometry may well be similar to that of the isobutyrate analogue as tin-carbon stretching region studies imply a non-linear Sn-C_2 skeleton as absorptions are observed at 560 and 523 cm^{-1} .

NMR examination of the material in a benzene solution revealed two resonances at 9.77 and 9.37 τ (Figure 37). The former peak is clearly due to methyltin protons as the usual symmetrically disposed spin-spin couplings were observed ($J=76.9\text{ cps}$). The 9.37 τ resonance is consequently assigned to the pivalate group protons. Integration of the respective signal intensities indicated a ratio of essentially 2/1. This ratio is in excellent agreement with the theoretical ratio of 2/1 predicted for a trinuclear species composed of two molecules of dimethylchlorotinpivalate and one molecule of dimethyltindipivalate. Based on this evidence the material is suggested to exist as a trinuclear methyltin carboxylate with the three tin atoms having formal coordination states of 5-6-5. The pivalate groups are suggested as being either symmetrically bridged or chelated and long-bonded bridging or chelating.

In summary, all of the unusual materials suggested as being trinuclear methyltin carboxylates, are believed to have similar structures. The greater magnitude of J observed in the isobutyrate and pivalate suggests a greater distortion from the tetrahedral angle than the formate. The excellent analytical data obtained for the formate and the consistent pattern of signal intensities observed in the NMR are believed to support the hypothesis that these three materials may be the first members of a new type of mixed methyltin carboxylate compounds. It is hoped that future workers will support or disclaim the proposed hypothesis by additional study of the reactions leading to these materials.

EXPERIMENTAL

Dimethylvinyltin Chloride.

A. Dimethyldivinyltin (20.3 g, 0.1 mole) diluted with about 100 ml of CHCl_3 was placed in a standard cold trap. The inlet side arm of the cold trap was connected to a tank of HCl through a safety flask. The exit arm of the cold trap was connected to an ascarite filled drying tube which led to a trap containing bromine (12.8 g, 0.08 mole) in CHCl_3 . The cold trap was maintained between 50-60°C by means of a steam bath. Hydrogen chloride was passed through the cold trap solution until the bromine solution was a pale yellow at which time the tubing connecting the ascarite-filled tube to the reactor burst, with an accompanying loss of an appreciable quantity of liquid from the reactor.

Solvent was flash distilled from the remaining liquid and the residual liquid distilled through an 18 inch Vigreux column at 10-12 mm pressure. Small amounts of two liquid fractions were obtained, (B.P. 51-56°C and B.P. 56-61°C). The pot residue solidified on cooling and a small amount of white solid was observed in the Vigreux column on cooling. Lit. B.P. 73-75°C @ 27 mm (73).

Vapor phase chromatography of the 51-56°C fraction indicated 8 components were present. (20% Dow Corning 710 fluid on chromosorb P. 6' x 1/4"; Helium carrier 43 ml/min., Injector 175°C, column 100-110°C, Detector 260°C, Nestor Faust prepchromat). Collection of the three most abundant components isolated trimethyltin chloride, dimethylvinyltin chloride and methyldivinyltin chloride, identified by NMR.

B. Dimethyltin dichloride (6.65 g, 30.2 mmole), dimethyldivinyltin (5 ml, ≈ 6.1 g, ≈ 31 mmole) and chloroform (30 ml) were combined in a 50 ml glass-stoppered Erlenmeyer flask and stirred magnetically. Initially a clear pale-yellow solution formed. Gas liquid chromatography of an aliquot after about 30 hours stirring indicated about 91-92% of the sample was a single component. (20% DC-11 on chromosorb P. 6' x 1/4", Helium carrier 60 ml/min., Injector 178°C, Column 110°C, Detector 260°C, attenuation 4, 2 μ l sample). Stirring an additional 12.5 hours increased the proportion of the major component to 94%. Further stirring failed to effect any further increase.

Preparative chromatography using a Nestor-Faust Prepkromat and a 6' x 1" column packed with 20% DC-710 fluid on chromosorb P isolated the major component; however, during the course of chromatography decomposition or further redistribution occurred, as the yield of product isolated was only 10-15% of that estimated by analytical chromatographic examination. The identity of the material was conclusively established as dimethylvinyltin chloride by NMR examination.

Dimethylchlorotin Formate.

Dimethylvinyltin chloride (2.277 g, 10.8 mmole), formic acid (0.4 ml, ≈ 0.5 g, ≈ 10.8 mmole) and dichloromethane (2 ml) were combined in a previously flamed 50 ml flask equipped with a condenser topped by a CaCl_2 drying tube. Gentle heating to remove solvent was begun after about three hours stirring at room temperature.

Purification was achieved by room temperature high vacuum sublimation to remove any solvent, unreacted formic acid or trimethyltin impurity followed by high vacuum sublimation at 77°C. The sublimer

was thoroughly cleaned between the two sublimations. All sublimer manipulations were carried out in a nitrogen filled glove bag protected with P_2O_5 . [Found: C, 15.52; H, 2.95; O, 13.74; Cl, 15.25. $ClC_3H_7O_2Sn$. Calcd: C, 15.72; H, 3.05; O, 13.96; Cl, 15.47%.]

Dimethylchlorotin Acetate.

Dimethyltin dichloride (15 g) and freshly distilled acetic anhydride (40 g, B.P. 130-133°C) were refluxed six hours. Excess liquid was removed by distillation (B.P. 110-125°C) and the flask connected to the high vacuum system through a sublimer. Room temperature sublimation for 20 hours produced 7.7 g of a white solid which smelled strongly of acetic acid. Continued sublimation using an oil bath heater (55°C initially, 95°C finally) resulted in 7.8 g of white sublimate which smelled of acetic acid and melted over the range 173-182°C.

Resublimation of the 7.8 g second crop of sublimate at room temperature resulted in 1.77 g of sublimate being harvested from the water cooled condenser and 1.06 g of white solid (M.P. 109-112°C) being collected from the liquid nitrogen cooled cold trap. Continued sublimation using a 90-100°C oil bath produced 2.78 g of white, crystalline solid. [Found: C, 19.97; H, 3.55; O, 13.01; Cl, 14.91. $ClC_4H_9O_2Sn$. Calcd: C, 19.75; H, 3.70; O, 13.16; Cl, 14.58%.] M.P. 180-182°C (Gallenkamp apparatus, sealed capillary).

About half the analytical sample (1.33 g) and 5 ml of spectro-quality cyclohexane were combined in a glass ampoule. The ampoule was degassed, sealed and heated about 13 hours in an oven (140-155°C). A few small black specks and a clear orange-yellow liquid were

present in the tube on removal from the oven. Beautiful yellowish-tan fern-like crystals formed on cooling. The solid was separated by filtration and then extracted with chloroform using a Soxhlet extractor. Tan and red-brown solid remained after removing the chloroform via a spin evaporator. The colored materials were dissolved in a small quantity of chloroform and the resulting solution concentrated until a very small quantity of bright orange liquid and a considerable crop of tan crystals remained. The clear orange liquid was decanted and subsequently examined by NMR and infrared spectroscopy.

Recrystallization of the tan solid using chloroform-pentane followed by sublimation at atmospheric pressure produced a white crystalline material. [Found: C, 19.90; H, 3.50; O, 13.04; Cl, 14.57. $\text{ClC}_4\text{H}_9\text{O}_2\text{Sn}$. Calcd: C, 19.75; H, 3.70; O, 13.16; Cl, 14.58%.] Molecular weight calcd: 243.2; found: 590 (13.457 mg/ml CH_2Br_2), 197 (10.566 mg/ml ethanol). M.P. 206-206.5°C (Gallenkamp apparatus, sealed capillary). Lit. (54) 189°C.

Dimethylchlorotindichloroacetate.

Dimethyltindichloride (3.649 g, 16.6 mmole), sodium dichloroacetate (5.184 g, 34.3 mmole) and butyl ether were combined in a 50 ml flask fitted with a condenser and the mixture refluxed four hours. Butyl ether was removed by vacuum distillation and the solid residue in the flask was slurried with a benzene pentane mixture. Filtration and vacuum sublimation of the solid produced a white solid which melted over a very broad range (80-120°C). Recrystallization from dichloromethane/pentane followed by high vacuum sublimation (90°C oil bath, 0.1 mm Hg) yielded the white crystalline analytical sample. [Found: C, 15.43; H, 2.76; O, 10.05; Cl, 33.78. $\text{Cl}_3\text{C}_4\text{H}_7\text{O}_2\text{Sn}$. Calcd: C, 15.38; H, 2.24; O, 10.25; Cl, 34.09%.]

Molecular weight calcd: 312.1; found: 373 (9.091 mg/ml CH_2Br_2);
151 (5.109 mg/ml ethanol).

Tetramethyl-1,3-dichlorodistannoxane.

The method of Okawara and Wada (72) was used. A solution of pyridine (3.9 g) in ethanol (30 ml) was added slowly to a magnetically stirred water solution of dimethyltin dichloride (11.0 g in 80 ml of water). The white precipitate which formed was washed several times with 95% ethanol and finally dried overnight in an oven at 105-110°C. [Found: C, 13.50; H, 3.36; O, 1.37; Cl, 12.04.

$\text{Cl}_2\text{C}_4\text{H}_{12}\text{O}_8\text{Sn}_2$. Calcd: C, 12.50; H, 3.12; O, 4.16; Cl, 18.45%.]

Trinuclear Methyltin Formate.

A. Material believed to be tetramethyl-1,3-dichlorodistannoxane (vide supra) (1.0 g) and 98% formic acid (10 g) were combined in a 50 ml flask fitted with a condenser and the mixture refluxed about 10 minutes. All of the white solid dissolved to form a clear colorless solution. Excess formic acid was removed by aspirator vacuum distillation followed by spin evaporation. The flask was heated by means of a hot-air gun during the spin evaporation step.

The flask was connected to the high-vacuum system through a sublimator fitted with a water cooled condenser. The non-melting white sublimate was submitted for elemental analysis without further purification. [Found: C, 17.24; H, 3.33; O, 18.33; Cl, 9.84.

$\text{Cl}_2\text{C}_{10}\text{H}_{22}\text{O}_8\text{Sn}_3$. Calcd: C, 17.21; H, 3.15; O, 18.36; Cl, 10.17%.]

A small sample of the above white solid sublimate was combined with spectro quality cyclohexane in a glass tube, the tube sealed and ultimately heated overnight in a 140°C oil bath. White solid

material was observed above the surface of the cyclohexane the following morning; therefore, the tube was placed in an oven (155°C) for about four hours additional heating. Long, white needles formed on the walls of the tube on cooling the clear, colorless solution. The tube was opened, the cyclohexane decanted and the solid dried with a slow stream of nitrogen. [Found. C, 17.24; H, 3.18; O, 18.33; Cl, 9.76. $\text{Cl}_2\text{C}_{10}\text{H}_{22}\text{O}_8\text{Sn}_3$. Calcd: C, 17.21; H, 3.15; O, 18.36; Cl, 10.17%.]

B. Dimethyltin dichloride (3 g, 13.7 mmole), sodium formate (0.74 g, 10.9 mmole) and formic acid (10 g, 21.7 mmole) were combined in a 50 ml flask fitted with a reflux condenser. Excess formic acid was removed by spin evaporation after the mixture was refluxed 1 1/4 hours. The flask was then connected to the high vacuum system through a sublimator. Room temperature sublimation (\approx 18 hours) resulted in 240 mg of white solid being recovered from the liquid nitrogen cooled cold trap. Immersion of the reaction flask in a 70°C oil bath and continued sublimation for four hours produced 822 mg of white powder retained on the water cooled probe, and 56 mg of white solid recovered from the cold trap. The bath temperature was increased to 105°C and sublimation was continued for nine hours at a pressure of about 0.4 mm Hg. White crystalline sublimate (3.286 g) and white powder (817 mg) were recovered from the condenser and cold trap respectively. Resublimation of the 105°C sublimate (3.286 g) produced the analytical sample. [Found: C, 17.33; H, 3.41; O, 18.25; Cl, 10.32. $\text{Cl}_2\text{C}_{10}\text{H}_{22}\text{O}_8\text{Sn}_3$. Calcd: C, 17.21; H, 3.15; O, 18.36; Cl, 10.17%.]

Trinuclear or Hexanuclear Methyltin Formate.

Material believed to be tetramethyl-1,3-dichlorodistannoxane (0.90 g, 2.34 mmole) was added to excess (10 g) hot formic acid and the resulting mixture refluxed for 10 minutes. Excess formic acid was removed from the clear colorless solution by vacuum distillation and the white solid residue sublimed under high vacuum directly from the flask onto an ice cooled sublimer condenser. The resulting sublimate started to melt at 95°C and continued to melt over a wide range. The melting point showed no improvement after three additional sublimations.

Cyclohexane (12 ml, Phillips) and sublimate (580 mg) were combined in a glass tube. The tube was thoroughly degassed, sealed and placed in a steam bath overnight. After about 12 hours heating, most of the material remained insoluble although a small amount of white solid was observed above the surface of the cyclohexane. A clear colorless solution resulted when the tube was heated about two days in a 150°C oven. White crystals formed on the walls of the tube on cooling to room temperature. The ampoule was opened, cyclohexane was decanted from the solid and the solid dried with a slow stream of dry nitrogen. [Found: C, 18.83; H, 3.20; O, 22.12; Cl, 4.05. $\text{ClC}_{11}\text{H}_{23}\text{O}_{10}\text{Sn}_3$ or $\text{Cl}_2\text{C}_{22}\text{H}_{46}\text{O}_{20}\text{Sn}_6$. Calcd: C, 18.68; H, 3.25; O, 22.64; Cl, 5.02%.] Molecular weight calcd: 706.5 or 1413; found: 1099.5 (7.037 mg/ml CH_2Br_2), 248 (2.534 mg/ml ethanol).

Trinuclear Methyltin Isobutyrate.

Dimethyltin dichloride (21.9 g, 0.1 mole), sodium isobutyrate (11.0 g, 0.1 mole) and butyl ether were combined in a 100 ml flask

equipped with a reflux condenser and the mixture refluxed about 2 1/2 days. A small amount of white insoluble material was present as well as a clear yellow solution. Most of the butyl ether was removed by spin evaporation with the flask being heated with a hot air gun. About 10-15 ml of liquid could not be removed, therefore the reaction flask was connected to the high vacuum system through a sublimator and high vacuum applied at room temperature for approximately 24 hours. Some white solid material sublimed and the liquid in the reaction flask was retained in the liquid nitrogen cooled cold trap. After thorough cleaning in a nitrogen filled glove bag protected with P_2O_5 , the sublimator was reconnected to the high vacuum system and the reaction flask immersed in an oil bath heated to 96°C. The white solid sublimate was not purified further. [Found: C, 26.10; H, 4.74; O, 10.09; Cl, 12.30. $ClC_6H_{13}O_2Sn$. Calcd: C, 26.57; H, 4.79; O, 11.81; Cl, 13.09%.]

Trinuclear Methyltin Pivalate.

Dimethyltin dichloride (11.0 g, 50 mmole), sodium pivalate (6.2 g, 50 mmole) and butyl ether (25 ml) were combined in a 100 ml flask equipped with a condenser and the magnetically stirred mixture refluxed 20 hours. Butyl ether was removed from the golden yellow solution by aspirator vacuum distillation. Benzene was added to the flask and the resultant solution filtered in a system protected from moisture.

A small amount of white solid separated from the golden-yellow benzene solution after two days cooling in a refrigerator. The solid was removed by filtration and the filtrate concentrated by spin evaporation. No additional solid formed, therefore hexane was added to

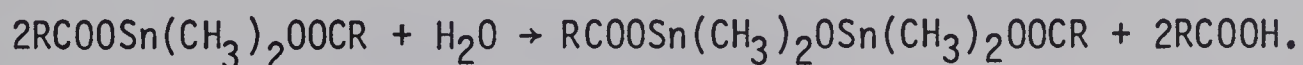
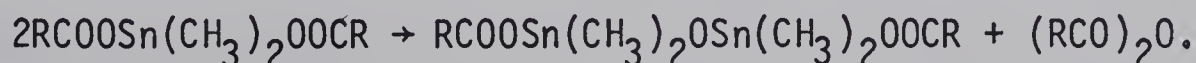
the residual liquid and the flask again cooled in a refrigerator. No solid was visible after two days cooling so the solvent was removed by spin evaporation and the flask connected to the high vacuum system through a sublimator. A considerable quantity of white solid sublimed from the flask which was immersed in an oil bath heated to about 45°C. NMR examination of the sublimate indicated the presence of an acidic proton so the material was carefully resublimed. Initially an air condenser was used in the sublimator and no heat applied to the material to be sublimed. After approximately 24 hours the sublimator was immersed in an oil bath heated to 59°C and water circulated through the sublimator condenser. Beautiful, clear, gem-like crystals were ultimately obtained.

CHAPTER V

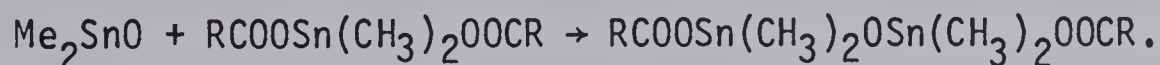
METHYLTIN CARBOXYLATE STANNOXANES

Methyltin carboxylate stannoxanes have not been investigated to any extent until very recently (6, 77). The vast majority of publications dealing with stannoxanes have been concerned with tetraalkyl-distannoxanes containing alkyl substituents larger than methyl, and non-carboxylate ligands. This chapter is concerned with the preparation and properties of methyltin carboxylate stannoxanes. The work described here is restricted to four materials containing different carboxylate moieties i.e., formate, pivalate, trichloroacetate and trifluoroacetate.

Methyltin carboxylate stannoxanes may be prepared by several different routes. Among the most common methods are the following. As was pointed out in Chapter III, hydrolysis or condensation of dimethyltin dicarboxylates can lead to tetramethyl-1,3-dicarboxylate distannoxanes.

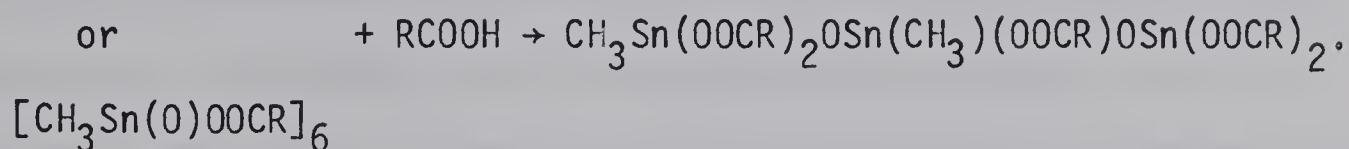
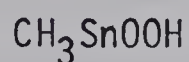


Also, dimethyltin oxide and dimethyltin dicarboxylates may be combined to form the desired tetramethyl-1,3-dicarboxylate distannoxane.



Methyltin carboxylate stannoxanes also result from the reaction

of methylstannonic acid (CH_3SnOOH) or a material formulated (78) as $[\text{CH}_3\text{Sn}(\text{O})\text{OCOR}]_6$ and an aliphatic carboxylic acid.



Tetramethyl-1,3-dicarboxylate distannoxanes are reported (77) to result from the reaction of carboxylic acids with an aqueous solution of dimethyltin dichloride in the presence of a deprotonating agent such as concentrated aqueous ammonia.

A recent review article (13) suggests that tetraalkyl 1,3-disubstituted distannoxanes exist as dimers in solution, with association occurring through tin-stannoxane oxygen coordinate bonds. Such a structure contains equal amounts of both four-coordinate and five-coordinate tin.

Attention is now directed to the materials prepared in this study. Although there are instances of similarity, each of the four different carboxylate-substituted methyltin substances will be discussed independently.

RESULTS AND DISCUSSION

Tetramethyl-1,3-diformoxy distannoxane.

Attempted synthesis of tetramethyl-1,3-diformoxy distannoxane from an aqueous solution of dimethyltin dichloride and formic acid using concentrated aqueous ammonia as the deprotonating agent resulted in the preparation of dimethyltin diformate. Isolation of this compound from an aqueous medium was rather startling in view of

the reported ease of hydrolysis of this compound (54). It is suggested that this observation supports the hypothesis advanced previously regarding decomposition of dimethyltin dicarboxylates: that hydrolysis of dimethyltin dicarboxylates undoubtedly results in the formation of tetramethyl-1,3-dicarboxylate distannoxanes, but the reaction is not rapid. Formation of the distannoxane by condensation must be considered to be of equal or even greater importance.

Tetramethyl-1,3-bis(pivaloxy)distannoxane.

A completely satisfactory elemental analyses was not obtained for this material. The sample analyzed correctly for carbon and hydrogen but low for oxygen; however, subsequent NMR studies (vide infra) left little doubt as to the identity of the material.

Molecular Weight Studies.

Tetramethyl-1,3-bis(pivaloxy)distannoxane appears to be a mixture of monomer (M.W. 515) and dimer (M.W. 1030) in dibromomethane solution with a rather peculiar concentration dependence. The molecular weight varies from 684 to 835 over the range 6.838 mg/ml - 32.718 mg/ml; however, it is not a smooth increase. The corresponding degree of association varies from 1.33 to 1.62 respectively. The molecular weight remains virtually constant (M.W. 804) over the middle portion of the concentration range studied (14.622 mg/ml - 21.578 mg/ml). In view of this behavior, meaningful extrapolation to infinite dilution is not possible.

The molecular weight exhibited by this compound is consistent with that of other distannoxanes containing potentially steric hindering groups. In addition, the electronegativity of the remaining

group and/or the availability of a suitable unshared pair of electrons may be important factors in the tendency for distannoxanes to dimerize. Examination of the molecular weights reported for some distannoxanes illustrated the point (Table XLII). The experimental evidence appears to support the concept of soluble distannoxanes existing in solution as an equilibrium mixture of monomeric and dimeric species, in contrast to the dimeric species as stated in a recent review article (13). NMR data (vide infra) support the equilibrium concept.

Infrared Spectra.

Complete infrared spectra data are given in Table XLIII.

Carbonyl-Carboxyl Region.

The most pronounced absorption observed (1550 cm^{-1}) occurs at essentially the same frequency in chloroform, cyclohexane, Nujol or KBr. The absence of an absorption near $1630\text{-}1660\text{ cm}^{-1}$ is taken to indicate the essentially complete bridging or chelation by the pivalate groups present. The relative simplicity of the spectrum in cyclohexane as contrasted to the multiplicity of shoulders and clearly defined peaks observed in the solid state and in polar solution may be indicative of intermolecular or intramolecular interactions in the latter instances, and essentially monomeric behavior in the former case. The previously discussed molecular weight data support a degree of aggregation in polar solution.

Tin-Carbon Stretching Region.

Non-linear C-Sn-C geometry appears to be indicated both in solution and in the solid state. Absorptions assignable to the asymmetric SnC_2 stretching mode are observed in the $570\text{-}580\text{ cm}^{-1}$ region while

TABLE XLII

MOLECULAR WEIGHTS FOR SOME DISTANNOXANES.

Compound	Method	M.W.	Degree of Association	Ref.
$\text{Et}_4\text{Sn}_2\text{Cl}_2\text{O}$	(1)	792	1.8	(79)
$\text{Et}_4\text{Sn}_2\text{Br}_2\text{O}$	(1)	904	1.7	(79)
$\text{Pr}_4\text{Sn}_2\text{Cl}_2\text{O}$	(1)	791	1.6	(80)
$\text{Pr}_4\text{Sn}_2\text{Br}_2\text{O}$	(1)	830	1.4	(79)
$\text{Pr}_4\text{Sn}_2(\text{NCS})_2\text{O}$	(1)	998	1.8	(81)
$\text{Bu}_4\text{Sn}_2\text{Cl}_2\text{O}$	(1)	1068	1.9	(80)
$\text{Bu}_4\text{Sn}_2\text{Br}_2\text{O}$	(2)	1170	1.8	(14)
$\text{Bu}_4\text{Sn}_2(\text{OAC})_2\text{O}$	(2)	1051	1.7	(14)

(1) Cryoscopically in benzene.

(2) Vapor pressure osmometer.

TABLE XLIII

INFRARED SPECTRA FOR TETRAMETHYL-1,3-BIS-PIVALOXYDISTANNOXANE

CHCl ₃	C ₆ H ₁₂	KBr	Nujol
	1635		
1613 sh		1615 m	1617 m
1605 m-s		1595 sh	1597 vw
1577 m		1575 sh	1575 sh
		1560 sh	1557 sh
1550 vs	1553	1552 s	1550 vs
1545 sh		1545 vs	1545 vs
			1532 sh
		1492 sh	
1481 s	1479	1478 s	1480 s
1462 w-m		1455 m	
		1442 w	
1418 m		1418 sh	1415 sh
		1412 s	1412 s
		1406 s	1408 s
1398 m	1392	1390 w	1392 vw
1378 w-m		1368 m	
1362 m		1358 m	
	1354	1352 m	
1345 m	1332	1330 m	1330 m
1235 w, br	1229	1220 m-s	1222 m-s
	1202	1203 w-m	1204 w-m
	1190	1192 w-m	1193 w-m
1030 vw		1024 w	1027 w
938 vw, br		933 w	937 vw
897 w		890 w-m	892 m
815 w, br			
	798	794 s	794 m-s
	790	787 s	787 m-s
	672	668 sh	662 sh
		660 sh	657 sh
645 m		648 sh	648 sh
642 sh	640	635 m-s	633 m-s
610 w-m			
604 sh	602	602 sh	605 sh
		596 m	599 m
577 w-m	575	570 m	575 m
		550 m	555 m
543 w		540 sh	545 sh
523 w		528 sh	525 sh
		520 w-m	519 m
505 w-m			502 sh
		497 m-s	495 m-s

absorption present in the $519\text{-}523\text{ cm}^{-1}$ region is attributed to the symmetric SnC_2 stretching mode.

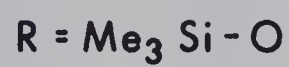
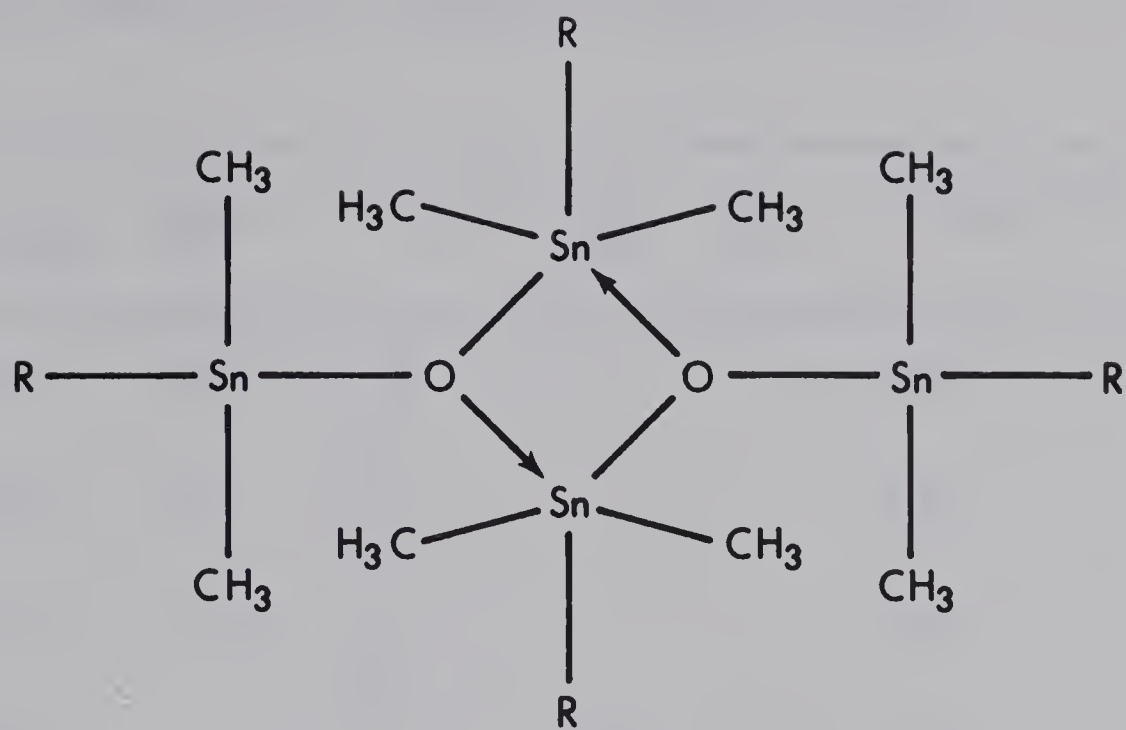
The non-linearity of the methyltin groups suggests that the monomeric distannoxane may exist as two trigonal bipyramids sharing an oxygen atom at one corner of each trigonal plane with a chelating carboxylate group and a cis arrangement of methyl groups about the tin atom.

The non-linear C-Sn-C skeleton revealed by the solid state spectrum is most likely due to associated molecules with a five-coordinate tin atom.

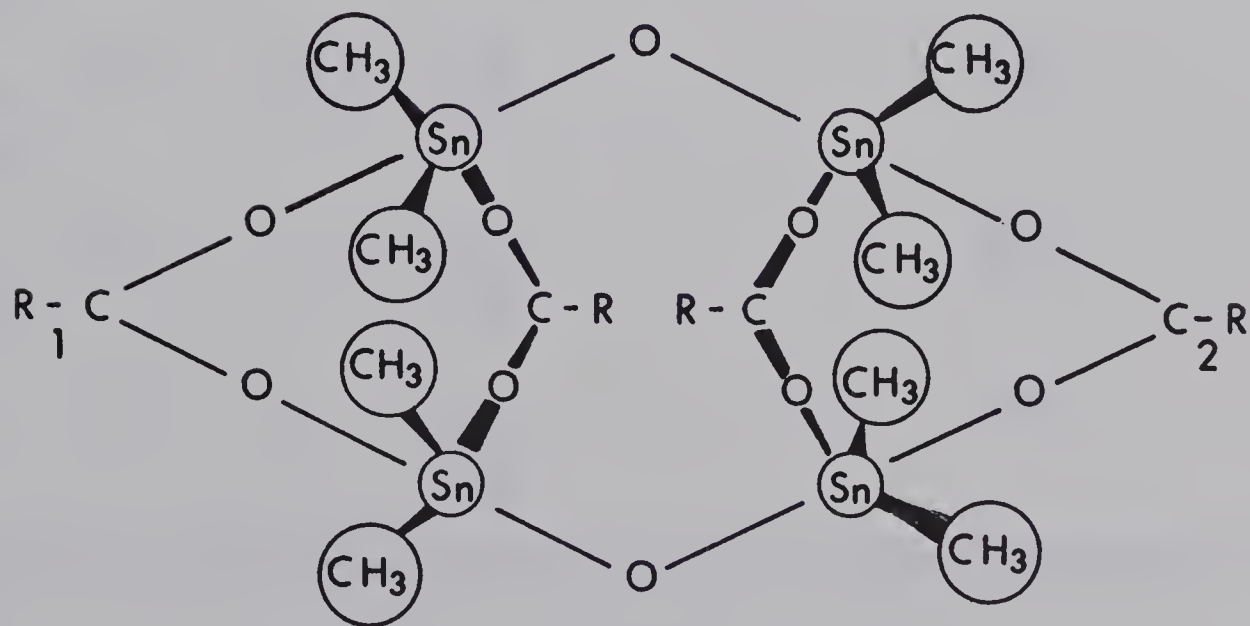
NMR Spectra.

Tetramethyl-1,3-bis(pivaloxy)distannoxane exhibits proton resonances at 9.30 and 9.25 τ due to the methyltin protons, and at 8.93 τ are due to pivalate groups (Table XLIV). The tin satellites corresponding to each methyltin resonance are very broad and not resolvable at room temperature or above, but are well resolved and identical at 0°C and below (J^1 90 cps; J^2 86.4 cps). Current opinion (13) holds that soluble distannoxanes exist as dimeric species in solution with both four- and five-coordinate tin being present in the dimer.

Davies et al. (14) found two methyltin resonances in $\text{Me}_4\text{Sn}_2\text{Cl}_2\text{O}$, and two different types of tin in a ^{119}Sn resonance study of $\text{Bu}_4\text{Sn}_2\text{X}_2\text{O}$ compounds. Okawara (12) determined from an x-ray analysis that tetramethyl-1,3-bis(trimethylsiloxy)distannoxane has a cyclic structure (XVIII) and is dimeric in the solid state. NMR study (69) of the compound revealed two distinct methyltin resonances of equal intensity each of which had a set of $\text{CH}_3\text{-Sn}$ couplings. The lower field signal couplings were larger ($J=82$ cps) than the higher field



XVIII



XIX

TABLE XLIV

PROTON MAGNETIC PARAMETERS FOR TETRAMETHYL-1,3-BIS PIVALOXY-DISTANNOXANE.

Solvent	Conc. mg/ml	Temp. °C	(CH ₃ -Sn)	J ¹ cps	J ² cps	[(CH ₃) ₃ COO]
{CDCl ₃ C ₆ H ₆	400	55	9.30 9.25			8.92
{CDCl ₃ C ₆ H ₆	400	50	9.30 9.25			8.93
{CDCl ₃ C ₆ H ₆	400	33.5	9.30 9.25			8.93
{CDCl ₃ C ₆ H ₆	400	0	9.33 9.27	90.2 90.2	86.4 86.4	8.95
{CDCl ₃ C ₆ H ₆	400	-25	9.33 9.29	89.3 89.3	85.8 85.8	8.96
{CDCl ₃ } 37.5 {C ₆ H ₆ } 37.5 {C ₅ H ₅ N} 62.5	400	+55	9.19 9.10			8.85
{CDCl ₃ } 37.5 {C ₆ H ₆ } 37.5 {C ₅ H ₅ N} 62.5	400	33.5	9.18 9.10			8.84
{CDCl ₃ } 37.5 {C ₆ H ₆ } 37.5 {C ₅ H ₅ N} 62.5	400	0	9.18 9.14 9.10			8.86
{CDCl ₃ } 37.5 {C ₆ H ₆ } 37.5 {C ₅ H ₅ N}	400	-25	9.18 9.14 9.10			8.87

signal couplings ($J=77.8$ cps). However, on heating the sample, the lower field signal decreased in intensity and finally disappeared entirely at 85°C leaving only the higher field four-coordinate tin methyl resonance.

A dimeric structure for tetramethyl-1,3-bis(pivaloxy)distanoxane such as XVIII is not consistent with the experimental evidence at hand. Assuming chelating carboxylate groups, such a structure would contain tin atoms with five and six nearest neighbors. It is not likely that the C-Sn-C angles would be essentially identical in both cases. The fact that the $\text{H}_3\text{C-Sn}$ couplings are of identical magnitude is believed to indicate that the methyl groups on tin have essentially identical C-Sn-C angles; however, the presence of two resonances indicates that they are in different magnetic environments.

A cis configuration of methyl groups about tin in a trigonal bipyramidal configuration with chelated carboxylate groups in equilibrium with a carboxylate bridged dimer having a cis arrangement of methyl groups is consistent with the observed facts. Variable temperature studies tend to confirm the hypothesis as the intensities of the two resonances remain equal although there is evidence of rapid exchange (Figure 38).

Complex Formation Studies.

Pyridine- d_5 addition causes a decrease in chemical shifts although the methyl-tin couplings are completely unresolvable. Interestingly enough, a third resonance, believed to be due to a methyl group on tin, is observed when the pyridine adduct is cooled to 0°C or below.

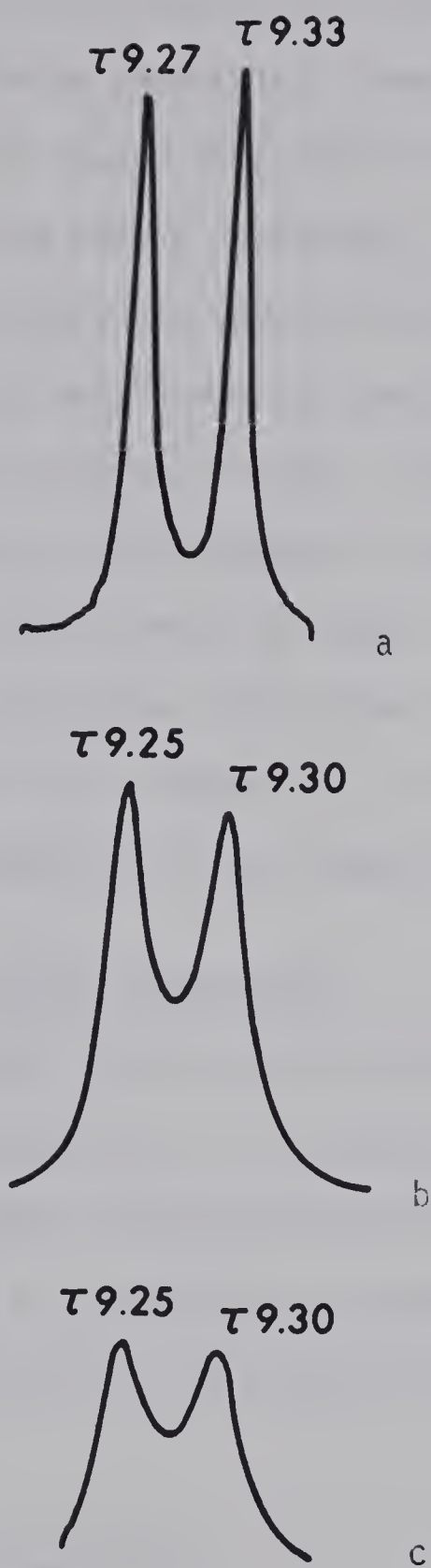


Figure 38. Variable temperature NMR of methyltin resonances of tetramethyl-1,3-bis(pivaloxy)distannoxane: a, 0°C; b, 33°C; c, +55°C.

The presence of two methyltin resonances with identical spin-spin couplings, completely associated carboxylate groups as indicated by infrared studies and a tendency toward dimerization may appear to be irreconcilable. Although it may appear unorthodox, a cyclic dimeric structure with bidentate carboxylate groups (XIX) in equilibrium with a monomeric chelated carboxylate group species would be consistent with the experimental evidence at hand. An important feature of these suggested structures is the presence of methyl groups in two differing magnetic environments which we refer to as "inner" and "outer" methyl groups. We prefer the "inner" and "outer" designation over the more usual "axial" and "equatorial" in view of the implied difference in bonding suggested by the latter designation.

Tetramethyl-1,3-bis(trichloroacetoxyl)distannoxane.

Isolation of this compound from the reaction of dimethyltin oxide and trichloroacetic acid was largely a fortuitous accident, as the reaction was designed to produce dimethyltinbis(trichloroacetate). The material is slightly soluble in chloroform as prepared. No attempt was made to increase the solubility by heating with cyclohexane.

Infrared Spectra.

Infrared data are listed in Table XLV.

Carbonyl-Carboxyl Region.

A single strong absorption (1670 cm^{-1}) is observed in the chloroform solution spectra of this compound. The frequency is close to that observed in trimethyltintrichloroacetate (1648 cm^{-1}) and tributyltintrichloroacetate (1646 cm^{-1}) (43). Assignment of this absorption to the asymmetric $\text{-CO}_2\text{-}$ stretching mode of an associated tri-

TABLE XLV

INFRARED SPECTRA FOR TETRAMETHYL-1,3-BIS(TRICHLOROACETOXY)
DISTANNOXANE.

CHCl ₃	Nujol
	1800 vw
1765 w	1695 s
1670 s	1665 s
1600 w-m	
	1515 w-m
1400 <u>sh</u>	1400 m
	1335 s
1318 s	
1306 s	1305 s
	1215 w
	1202 m
	962 m
945 w	945 w-m
	850 s
840 <u>sh</u>	838 s
835 <u>s</u>	
	748 s
	680 s
625 w, br	
570 m	

chloroacetate group is relatively certain. Due to the lack of molecular weight studies, no choice may be made between chelated or bridged trichloroacetate groups. The corresponding symmetric $\text{-CO}_2\text{-}$ stretching mode is observed as a broad peak ($1318\text{-}1306\text{ cm}^{-1}$) which may be a doublet.

Absorptions in the solid state are quite similar to those observed in chloroform solution. Strong and broad absorptions at $1695\text{-}1665\text{ cm}^{-1}$ and $1335\text{-}1305\text{ cm}^{-1}$ are assigned to asymmetric and symmetric stretching modes respectively. The lack of a significant absorption in the $1710\text{-}1700\text{ cm}^{-1}$ region is believed to be conclusive proof of the absence of free ester-like trichloroacetate groups.

Tin-Carbon Stretching Region.

Observation of a single absorption (570 cm^{-1}) assignable to the asymmetric stretching mode of a SnC_2 skeleton suggests a linear C-Sn-C skeleton exists in this compound.

NMR Spectra.

Due to the low solubility of tetramethyl-1,3-bis(trichloroacetoxy)distannoxane in chloroform, NMR spectra were obtained with warmed solutions and a Varian C-1024 CAT (Time Averaging Computer). Two methyltin signals are observed at 8.83 and 8.93τ (Table XLVI). Each resonance is accompanied by a set of spin-spin couplings; however, unlike the pivaloxy analogue, they are of slightly different magnitude. Couplings of 87.5 cps are observed with the 8.83τ resonance while the 8.93τ resonance is accompanied by couplings of 84.5 cps . This observation is similar to that mentioned previously for tetramethyl-1,3-bis(trimethylsiloxy)distannoxane and may indicate a somewhat analogous structure.

TABLE XLVI

PROTON MAGNETIC PARAMETERS FOR
TETRAMETHYL-1,3-BIS(TRICHLOROACETOXY)DISTANNOXANE.

$\text{CH}_3\text{-Sn}$ ζ	J^1 cps	J^2 cps	$\text{CH}_3\text{-Sn}$ ζ	J^1 cps	J^2 cps	Temp.
8.83	87.5	84.0	8.93	84.5	80.8	60°C

23 CAT SCANS.

The following proposed structure is believed to be consistent with the available facts. Association through stannoxane oxygen-tin bonds with chelated trichloroacetate groups would produce a cyclic dimer with essentially trigonal-bipyramidal end groups. The tin atoms of the four-membered ring would be surrounded by six nearest neighbors. These units may be viewed as octahedral. Thus, the dimer would have both trigonal bipyramidal and octahedral components. It is not unreasonable to assume that the C-Sn-C angle of an octahedral arrangement would be closer to linear than that present in a trigonal-bipyramid in view of the greater degree of crowding which exists in an octahedron. If this assumption is valid, the difference in couplings may be explained by a slightly greater C-Sn-C angle present in the units making up the cyclic portion of the molecule.

Hexamethyl-bis(trifluoroacetoxy)tristannoxane.

Polymeric dimethyltin stannoxanes containing carboxylate groups have not been reported. The material discussed here was obtained in very low yield from a preparation designed to afford dimethyltinbis-trifluoroacetate. The white powdery compound sublimed at 180°C at high vacuum. Due to its low solubility in chloroform, NMR examination was omitted. Instead, mass spectrometer examination was used to confirm the identity of the material.

Infrared Spectra.

Hexamethyl-bis(trifluoroacetoxy)tristannoxane is sufficiently soluble in chloroform to allow the use of solution infrared spectroscopy. Complete data are given in Table XLVII.

TABLE XLVII

INFRARED SPECTRA FOR HEXAMETHYL-BIS(TRIFLUOROACETOXY)TRISTANNOXANE.

CHCl ₃	Nujol
1712 sh	1785 <u>sh</u> 1710 <u>s</u> 1700 s
1685 sh	
1678 s	1670 s
1666 s	1660 s
1650 sh	
	1622 <u>sh</u> 1585 <u>m</u>
1555 vw	
1460 vw	
1455 vw	
1423 sh	1420 s
1400 <u>sh</u>	
1375 <u>m</u>	
1315 s	
1310 s	
	1230 s
1172 sh	
1152 m	1140 s
946 m	
840 sh	850 m-s
835 s	
788 sh	790 s
765 w-m	
680 w	
640 w-m	635 s
570 w-m	
518 w	

Carbonyl-Carboxyl Region.

Strong absorptions are observed at 1678 and 1666 cm^{-1} in the chloroform solution spectrum of this compound. Shoulders at 1712 and 1685 cm^{-1} precede these strong absorptions. Assignment of these absorptions is in large measure uncertain. Free ester-like trifluoroacetate groups on tin have been reported (44) to absorb near 1720 cm^{-1} and therefore it is not unreasonable to assign the 1712 cm^{-1} shoulder to an unassociated trifluoroacetate group. Judging from the frequency of the strongest absorptions, it is evident that some type of association is occurring in solution. We offer no choice between long-bonded or symmetrical chelation or bridging, as both forms could account for the decrease in the asymmetric $\text{-CO}_2\text{-}$ frequency. Absorptions reasonably assigned to the corresponding symmetric $\text{-CO}_2\text{-}$ absorptions are observed at 1315 and 1310 cm^{-1} .

Nujol mull spectra are slightly more complex and indeed rather puzzling. Two sets of strong absorptions are observed at 1710 and 1700 cm^{-1} and at 1670 and 1660 cm^{-1} . Assignment of the 1670 and 1660 cm^{-1} peaks to some type of associated trifluoroacetate group is consistent with the suggestions outlined in the solution spectrum discussion. The intensity and frequency of the 1710 and 1700 cm^{-1} absorptions are puzzling. Normally, association would be expected to predominate in the solid state; therefore, the appearance of these bands at a frequency intermediate between a presumably free ester-like trifluoroacetate group and what has been suggested as some type of bridged trifluoroacetate group suggests significant structural changes occur on dissolution in chloroform.

Tin-Carbon Stretching Region.

Apparently at least one SnC_2 unit exists as a non-linear C-Sn-C skeleton as absorptions assignable to asymmetric and symmetric tin-carbon stretching modes are observed at 570 and 518 cm^{-1} in chloroform solution.

Mass Spectrometric Study.

High resolution mass spectroscopy provided strong evidence that the compound was indeed a hexamethyl-bis(trifluoroacetoxy)tristannoxane. The cracking pattern is complicated by the large number of tin isotopes; however, seven different organotin fragments were readily identified (Table XLVIII). Although the molecular ion was not observed, the presence of an ion of M/e 689 (consistent with pentamethylbis(trifluoroacetoxy)tristannoxane) and the excellent agreement between the experimental (590.8239) and theoretical (590.8223) M/e of hexamethyltrifluoroacetoxytristannoxane are believed to establish the identity of the compound.

TABLE XLVIII

PRINCIPLE MASS SPECTRAL FRAGMENTS

HEXAMETHYL BIS(TRIFLUOROACETOXY)TRISTANNOXANE.

Nominal Observed Mass M/e	Elemental Composition	Relative Intensity
689	$C_9F_6H_{15}O_6Sn_3$	(46.5)
591 (a)	$C_8F_3H_{18}O_4Sn_3$	(20.6)
479	$C_5H_{15}O_3Sn_3$	(27.2)
427	$C_6F_3H_{12}O_3Sn_2$	(36.8)
361	$C_5F_6H_3O_4Sn$	(18.1)
335	$C_2F_6HO_4Sn$	(22.8)
263	$C_4F_3H_6O_2Sn$	(100)

(a) Exact mass found: 590.8239.
Calculated exact mass: 590.8223.

EXPERIMENTAL

The method of Ohara, et. al. (77) was used.

Tetramethyl-1,3-bis(formoxy)distannoxane.

Concentrated aqueous ammonia was added dropwise to a magnetically stirred solution of dimethyltindichloride (5 g, 22.8 mmoles) and formic acid (4 g, 86.9 mmoles) in 100 ml of water. Addition was continued until no further precipitate formed. The white solid was isolated by filtration, washed with a small amount of dilute aqueous formic acid and then a small quantity of methanol and dried in vacuo. Final purification was accomplished by recrystallization from methanol containing a small amount of formic acid. [Found; C, 20.09; H, 3.47; O, 26.91. Calcd: for tetramethyl-1,3-diformoxydistannoxane $C_6H_{14}O_5Sn_2$. C, 17.86; H, 3.50; O, 19.85%; Dimethyltindi-formate, $C_4H_8O_4Sn$. Calcd: C, 20.11; H, 3.35; O, 26.81%.]

Tetramethyl-1,3-bis(pivaloxy)distannoxane.

Dimethyltindichloride (5 g, 22.8 mmoles) and pivalic acid (8.87 g, 86.9 mmoles) were dissolved in 100 ml of water. Concentrated aqueous ammonia was added dropwise to the magnetically stirred solution until no further white precipitate formed. The white solid was separated by filtration, washed with a small quantity of water and then with a small quantity of methanol containing a small quantity of pivalic acid. After drying in a vacuum dessicator, the material was recrystallized from methanol containing a trace of pivalic acid and again dried in a vacuum dessicator. [Found: C, 32.20; H, 5.97; O, 13.33. $C_{14}H_{30}O_5Sn_2$. Calcd: C, 32.62; H, 5.82; O, 15.53%.]

Molecular weight 684 (6.838 mg/ml CH_2Br_2), 803 (14.622 mg/ml CH_2Br_2), 805 (21.578 mg/ml CH_2Br_2), 835 (32.718 mg/ml CH_2Br_2).

Tetramethyl-1,3-bis(trichloroacetoxy)distannoxane.

Dimethyldivinyltin (1.00 g, ≈ 5 mmoles) was added to trichloroacetic acid (1.58 g, 9.7 mmoles) in a 50 ml round bottom flask fitted with a reflux condenser topped with a CaCl_2 drying tube. The assembled apparatus was thoroughly flamed prior to use. Vigorous bubbling began immediately on adding the dimethyldivinyltin and the flask became very hot. A clear brown liquid was present after bubbling ceased. The light brown solid which formed on cooling to room temperature was completely soluble in dichloromethane. The resulting solution was filtered in an apparatus protected from moisture, petroleum ether was added and the flask placed in a freezer. The white solid which had formed on cooling overnight was separated by filtration in an apparatus protected from moisture and the solid washed with pentane. The washing operation was also conducted in an apparatus protected from moisture. Recrystallization from dichloromethane/petroleum ether and drying in a vacuum dessicator yielded the analytical sample. [Found: C, 15.19; H, 1.96; O, 12.68; Cl, 33.18. $\text{Cl}_6\text{C}_8\text{H}_{12}\text{O}_5\text{Sn}_2$. Calcd: C, 15.05; H, 1.88; O, 12.53; Cl, 33.33%.] M.P. 209-211°C.

Hexamethyl-bis(trifluoroacetoxy)tristannoxane.

Dimethyldivinyltin (2 ml, ≈ 2.5 g, ≈ 12.3 mmole) and dichloromethane (10 ml) were combined in a 100 ml 3-neck flask equipped with a dropping funnel, condenser topped with a CaCl_2 drying tube and a nitrogen inlet. The apparatus was thoroughly flamed prior to use.

Trifluoroacetic acid (1.83 ml, \approx 2.8 g, \approx 24.6 mmole) diluted with dichloromethane (10 ml) was added slowly drop by drop to the magnetically stirred solution. White solid formed on adding the acid. The flask was attached to the high vacuum system through a sublimator and high vacuum applied at room temperature for five hours. A small amount of white solid was observed on the air cooled condenser. The sublimator was transferred to a nitrogen filled glove bag protected with P_2O_5 , the sublimate removed, the sublimator thoroughly cleaned, reassembled, and ultimately reconnected to the high vacuum system. Continued high vacuum sublimation using a water cooled condenser and a 77°C oil bath produced a considerable quantity of white sublimate. The initial sublimate was rejected without examination. Resublimation of the 77°C sublimate was carried out in three stages with sublimate removal and thorough cleaning between stages. Initially, room temperature high vacuum sublimation produced a very small amount of white solid which was rejected without examination. A small quantity (10-20%) of solid remained in the sublimator after continued sublimation at \approx 70°C. Therefore, the temperature was increased to 180°C. All remaining solid sublimed. The 180°C sublimate was examined without further manipulation. [Found: C, 17.80; H, 2.37; F, 16.75.

$C_{10}F_6H_{18}O_6Sn_3$. Calcd: C, 17.04; H, 2.55; F, 16.19%.]

Mass spectral information was obtained with the MS-9 spectrometer. Direct probe, source temperature 200°C. Electron energy 100 volts, trap current 100 microamps.

APPENDIX

Evolution of the Problem and Interesting Miscellaneous Observations.

Methylmanganese pentacarbonyl and acetylmanganese pentacarbonyl may be interconverted by several routes. Carbon monoxide (82, 83) or a ligand such as triphenylphosphine or an amine (84) can transform methylmanganese carbonyl into acetylmanganese carbonyl. Originally, the objective of this research was to determine if a CO molecule could be "inserted" into the metal-metal bond of trimethyltinmanganese pentacarbonyl. Reaction of trimethyltinmanganese pentacarbonyl and cyclohexylamine in tetrahydrofuran (THF) produced a color change from yellow to orange. Infrared examination in cyclohexane of the orange oil which remained after removal of the THF indicated a new absorption at 1680 cm^{-1} ; however, the presence of absorptions near 1630 cm^{-1} in cyclohexylamine was believed to cast uncertainty on the nature of the 1680 cm^{-1} band. Sublimation and column chromatography on alumina failed to isolate a product containing both carbonyl bands (2000 cm^{-1} region) and the new 1680 cm^{-1} band. Repetition of the experiment using triphenylphosphine in place of cyclohexylamine again produced new bands; however, the results were inconclusive.

Reaction of trimethyltinmanganese pentacarbonyl in cyclohexane with high pressure carbon monoxide produced new bands at 1728 and 1585 cm^{-1} ; however, no solid material could be isolated which contained either of these bands.

Due to difficulties encountered with trimethyltinmanganese pentacarbonyl a simpler system containing a metal-metal bond was sought. Hexamethylditin was chosen because it was on hand and it

contained the trimethyltin moiety. Reaction of clear, colorless hexamethylditin, as received from M&T Chemicals, with high pressure CO in spectral quality cyclohexane at about 80°C, produced a very small quantity of fine white needles. The observation of white needles on the closing plate was indeed surprising. Ultimately, the material was identified conclusively (elemental analysis, NMR, IR, Molecular weight) as trimethyltin formate. Reproducibility was demonstrated repeatedly although the yield was always very low. Formation of trimethyltin formate from CO and material believed to be hexamethylditin seemed to border on alchemy.

Subsequently it was demonstrated that very little trimethyltin-formate formed if the "hexamethylditin" was freshly distilled. Attempted determination of peroxides (85) in the tin compound failed as the control sample indicated a higher peroxide content than the sample. It is thus apparent that the hexamethylditin used in this study contained some material or materials capable of forming trimethyltin-formate with carbon monoxide.

Before discovering the procedure for solubilizing insoluble trimethyltin-formate, the soluble formate was produced from carbon monoxide and trimethyltin chloride, and from trimethyltin hydride and carbon monoxide.

During the course of this study, redistribution of methyl groups bonded to tin has been observed repeatedly. Redistribution was most pronounced when dimethyldivinyltin was used as a starting material, although there were other cases where NMR evidence indicated redistribution.

Very little research regarding the thermal decomposition of organotin compounds has been reported. Quite recently, Ohara and Okawara (86) reported that tri-n-propyltin formate and tri-n-butyltin formate may be thermally decomposed to yield the corresponding tin hydride.

It is possible that dimethyltin carboxylates may undergo a thermal redistribution to yield trimethyltin carboxylates and methyltin tricarboxylates although at this time this suggestion must be considered highly speculative.

No NMR spectra of methylvinyltin compounds have appeared in the literature; therefore, the spectrum of the crude reaction product of dimethyldivinyltin and dimethyltin dichloride (Figure 39), and the compounds isolated from the crude product (trimethyltin chloride, Figure 40; dimethylvinyltin chloride, Figure 41; and methyldivinyltin chloride, Figure 42) are given for the benefit of future workers.

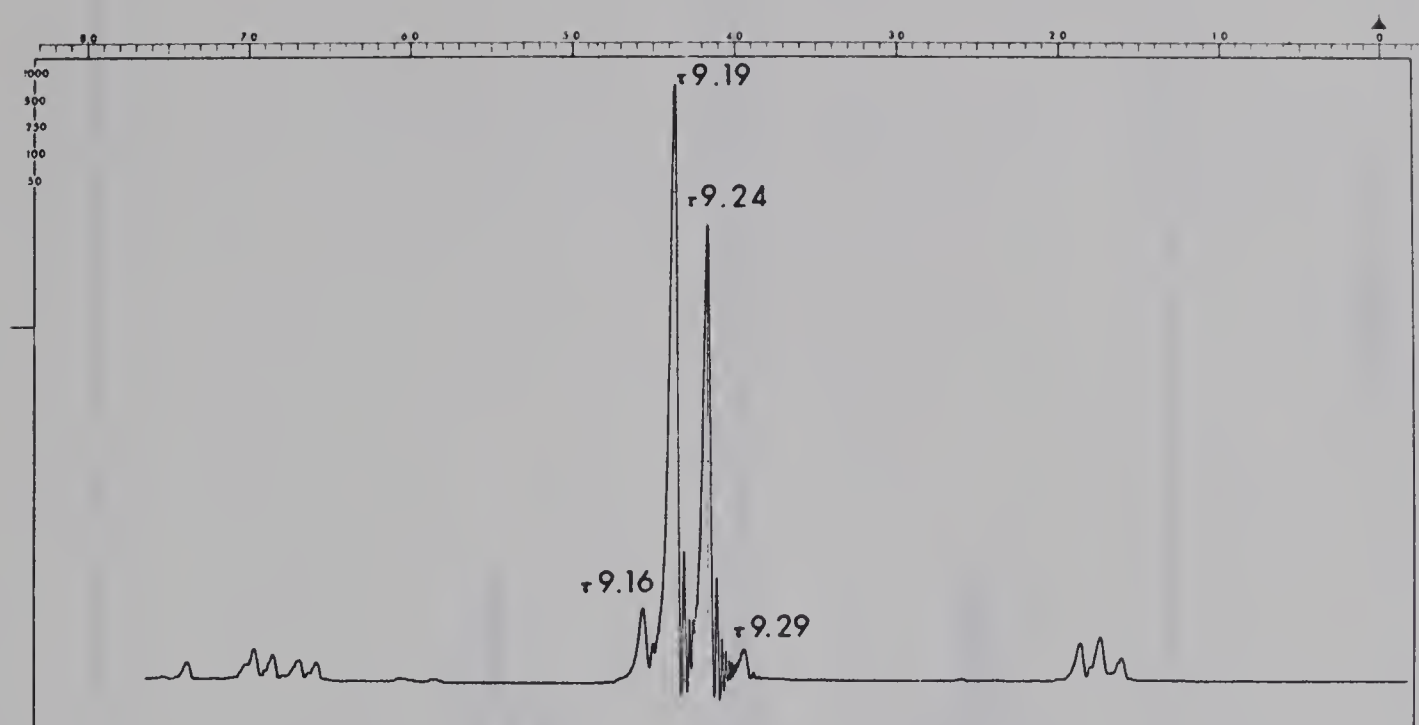


Figure 39. NMR spectrum of dimethyldivinyltin/dimethyltin dichloride redistribution reaction product.

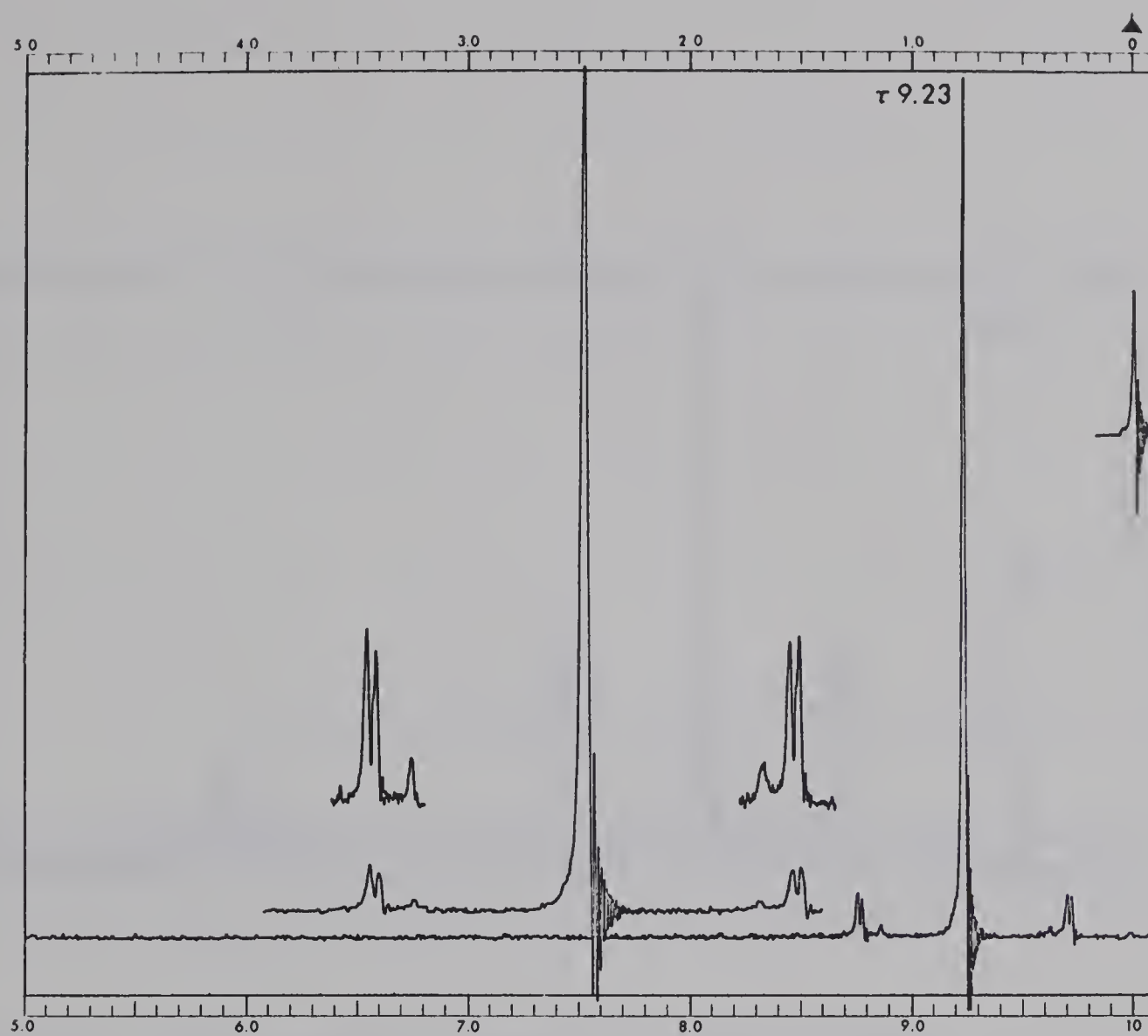


Figure 40. NMR spectrum of trimethyltin chloride.

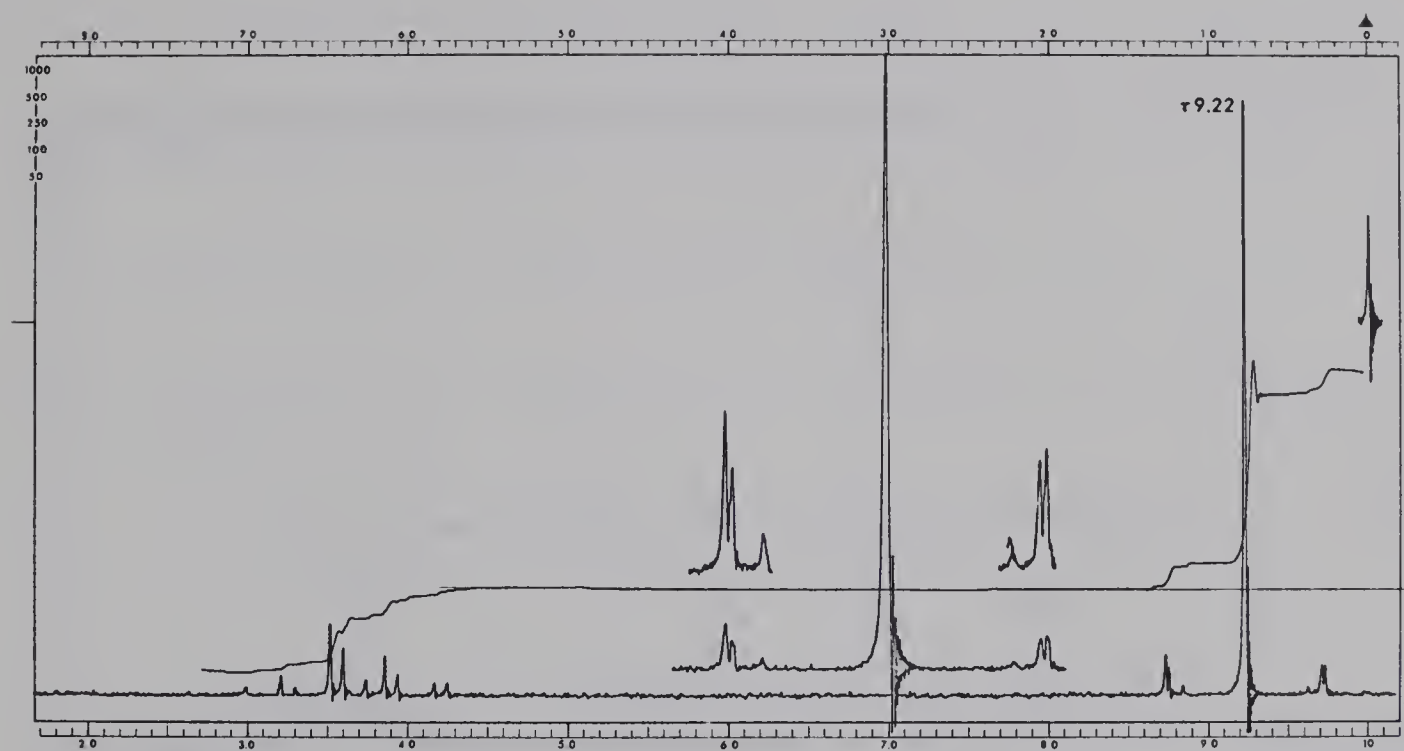


Figure 41. NMR spectrum of dimethylvinyltin chloride.

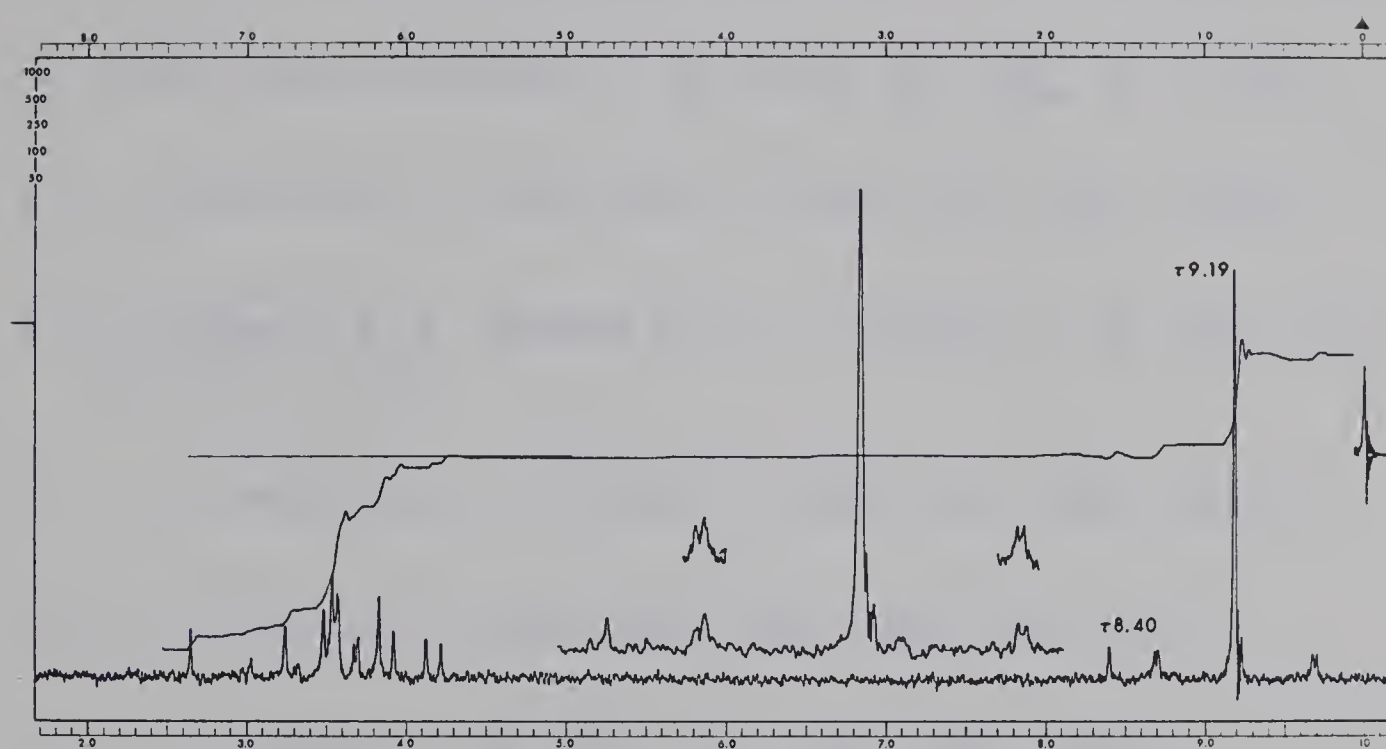


Figure 42. NMR spectrum of methyldivinyltin chloride.

BIBLIOGRAPHY

1. R. K. Ingham, S. D. Rosenberg and H. Gilman, Chem. Rev., 60, 459, (1960).
2. D. H. Olson and R. E. Rundle, Inorg. Chem., 2, 1310, (1963).
3. W. P. Neumann, Angewandte Chemie, Intern. Ed., 2, 165, (1963).
4. West, Baney and Powell, J. Am. Chem. Soc., 82, 62, (1960).
5. J. Chatt and A. A. Williams, J. Chem. Soc., 4403, (1964).
6. R. Okawara, D. E. Webster and E. G. Rochow, J. Am. Chem. Soc., 82, 3287, (1960).
7. I. R. Beattie and T. Gilson, J. Chem. Soc., 2585, (1961).
8. R. C. Poller, J. Inorg. Nucl. Chem., 24, 593, (1962).
9. J. P. Freeman, J. Am. Chem. Soc., 80, 5954, (1958).
10. M. Wada, M. Shindo and R. Okawara, J. Organometal. Chem., 1, 95, (1963).
11. R. Okawara, Proc. Chem. Soc., 383, (1961).
12. R. Okawara, N. Kasai and K. Yasuda, 2nd Intern. Symp. Organometal. Chem., Wisconsin, p. 128, (1965).
13. R. Okawara and M. Wada in "Advances in Organometallic Chemistry", F. G. A. Stone and Robert West, Editors, Vol. IV, Academic Press, New York, 1966, p. 137.
14. D. L. Alleston, A. G. Davies, M. Hancock and R. F. M. White, J. Chem. Soc., 5469, (1963).

15. M. L. Maddox, N. Flitcroft and H. D. Kaesz, J. Organometal. Chem., 4, 50, (1965).
16. N. A. Matwiyoff and R. S. Drago, Inorg. Chem., 3, 337, (1964).
17. I. R. Beattie, G. P. McQuillan and R. Hulme, Chem. Ind.(London), 1429, (1962).
18. Craig, Maccoll, Nyholm, Orgel and Sutton, J. Chem. Soc., 332, (1954).
19. I. R. Beattie and G. P. McQuillan, J. Chem. Soc., 1519, (1963).
20. M. M. McGrady and R. S. Tobias, J. Am. Chem. Soc., 87, 1909, (1965).
21. R. J. Gillespie, J. Chem. Educ., 40, 295, (1963).
22. R. Newman, J. Chem. Phys., 20, 1663, (1952).
23. K. Ito and H. J. Bernstein, Can. J. Chem., 34, 170, (1956).
24. G. J. M. van der Kerk, J. G. A. Luijten and M. J. Janssen, Chimia, 16, 10, (1962).
25. G. J. M. van der Kerk, J. G. A. Luijten and M. J. Janssen, Rec. Trav. Chim., 82, 90, (1963).
26. R. A. Cummins and P. Dunn, Australian J. Chem., 17, 185, (1964).
27. R. Okawara and M. Ohara, J. Organometal. Chem., 1, 360. (1964).
28. R. Okawara and M. Ohara, Bull. Chem. Soc. Japan, 36, 623, (1963).
29. L. J. Bellamy in THE INFRARED SPECTRA OF COMPLEX MOLECULES, Methuen and Co. Ltd., London, 2nd Ed., (1958).

30. H. G. Langer and A. H. Blut, J. Organometal. Chem., 5, 291, (1966).
31. N. Mueller, J. Chem. Phys., 36, 359, (1962).
32. J. R. Holmes and H. D. Kaesz, J. Am. Chem. Soc., 83, 3903, (1961).
33. J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry", Tin Research Institute, England, (1955).
34. G. Bor and L. Marko, Spectrochim. Acta., 16, 1105, (1960).
35. Y. Maeda, C. R. Dillard and R. Okawara, Inorg. Nucl. Chem. Letters, 2, 197, (1966).
36. Y. Kawasaki and T. Tanaka, J. Chem. Phys., 43, 3396, (1965).
37. J. A. S. Smith and E. J. Wilkins, J. Chem. Soc. (A), 1749, (1966).
38. J. W. Faller and A. Davidson, Inorg. Chem., 6, 182, (1967).
39. F. P. Boer, J. J. Flynn, H. H. Freedman, S. V. McKinley and V. R. Sandell, J. Am. Chem. Soc., 89, 5068, (1967).
40. F. P. Boer and H. H. Freedman, Personal Communication to Professor W. A. G. Graham.
41. M. Elder, W. A. G. Graham, D. Hall and R. Kummer, Unpublished work.
42. P. B. Simons and W. A. G. Graham, J. Organometal. Chem., 8, 479, (1967).
43. R. A. Cummins, Australian J. Chem., 17, 594, (1964).

44. M. Vilarem and J. C. Maire, Compt. Rend. Ser. C., 262, 480, (1966).
45. P. B. Simons and W. A. G. Graham, J. Organometal. Chem., 10, 457, (1967).
46. J. G. A. Luijten, Rec. Trav. Chim., 82, 1179, (1963).
47. C. A. Craus and R. H. Bullard, J. Am. Chem. Soc., 51, 3605, (1929).
48. A. Cahours, Ann., 114, 354, (1860).
49. T. Harada, Bull. Chem. Soc., Japan, 17, 283, (1942).
50. T. Harada, Sci. Papers Inst. Phys. Chem. Res., Tokyo, 42, 57, (1947); C. A. 43, 7899, (1949).
51. H. Sato and R. Okawara, International Symposium on Molecular Structure and Spectroscopy, Tokyo, (1962).
52. Y. Maeda and R. Okawara, J. Organometal. Chem., 10, 247, (1967).
53. W. Kitching, J. Organometal. Chem., 6, 586, (1966).
54. R. Okawara and E. G. Rochow, J. Am. Chem. Soc., 82, 3285, (1960).
55. L. A. Duncanson, W. Gerrard, M. F. Lappert, H. Pyszora and R. Shafferman, J. Chem. Soc., 3652, (1958).
56. V. G. Kumar Das and W. Kitching, J. Organometal. Chem., 10, 59, (1967).
57. M. Shindo and R. Okawara, Inorg. Nucl. Chem. Letters, 3, 75, (1967).
58. W. Kitching, Tetrahedron Letters, 31, 3689, (1966).

59. G. P. van der Kelen, *Nature*, 193, 1069, (1962).
60. D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, 87, 3994, (1965).
61. W. McFarlane, *J. Chem. Soc. (A)*, 528, (1967).
62. E. O. Schlemper, *Inorg. Chem.*, 6, 2012, (1967).
63. A. H. Westlake and D. F. Martin, *J. Inorg. Nucl. Chem.*, 27, 1579, (1965).
64. W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, 27, 89, (1965).
65. K. Kawakami and R. Okawara, *J. Organometal. Chem.*, 6, 249, (1966).
66. R. S. Tobias and C. E. Freidline, *Inorg. Chem.*, 4, 215, (1965).
67. R. S. Tobias, H. N. Farrer, M. B. Hughes and B. A. Nevett, *Inorg. Chem.*, 5, 2052, (1966).
68. A. Sitow, E. G. Rochow and D. Seyferth, *J. Org. Chem.*, 23, 116, (1958).
69. W. J. Considine, G. A. Baum and R. C. Jones, *J. Organometal. Chem.*, 3, 308, (1965).
70. D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, 79, 515, (1957).
71. R. Jacob, *Bull. Chem. Soc. France*, 7, 581, (1940).
72. R. Okawara and M. Wada, *J. Organometal. Chem.*, 1, 81, (1963).
73. D. Seyferth, *J. Am. Chem. Soc.*, 79, 2133, (1957).

74. W. Jetz, P. B. Simons, J. A. J. Thompson and W. A. G. Graham, Inorg. Chem., 5, 2217, (1966).
75. A. G. Davies and P. G. Harrison, J. Organometal. Chem., 7, P13, (1967).
76. A. G. Davies, P. G. Harrison and P. R. Palan, J. Organometal. Chem., 10, P33, (1967).
77. M. Ohara, R. Okawara and Y. Nakamura, Bull. Chem. Soc. Japan, 38, 1379, (1965).
78. H. H. Anderson, Inorg. Chem., 3, 912, (1964).
79. Pfieffer and Brack, Z. Anorg. Chem., 87, 229, (1914).
80. Johnson and Fritz, J. Org. Chem., 19, 74, (1954).
81. Wada, Nishing and Okawara, J. Organometal. Chem., 3, 70, (1965).
82. T. H. Coffield, R. D. Closson and J. Kozikowski, J. Org. Chem., 22, 598, (1957).
83. F. Calderazzo and F. A. Cotton, Inorg. Chem., 1, 30, (1962).
84. R. J. Mawby, F. Basolo and R. G. Pearson, J. Am. Chem. Soc., 86, 3994, (1964).
85. Davies, J. Chem. Soc., 1550, (1958).
86. M. Ohara and R. Okawara, J. Organometal. Chem., 1, 360, (1964).

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